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The Production and Properties of

PLASTICS

By

S. LEON KAYE

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International Textbook Company

Scranton, Pennsylvania

1947

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Preface

Today the word *plastics* is used with the same inflection and apparent knowledge as the words refrigerator and automobile. Women see and use plastics in the kitchen, as cosmetic and make-up accessories, and as clothing. Children's nurseries and toy departments are well stocked with plastics. Business men see and use plastics in their businesses, as well as in many useful household gadgets. To the uninitiated, the word plastic seems to connote anything from a pin point to an aeroplane. The remark so frequently made, "Oh! that's plastic," clearly shows that the public eye has been caught by plastic fancy. Truly, then, America's infant industry has come of age.

One of the main reasons for this sudden seeming interest in plastics is the tremendous increase of visible applications of plastic materials. In the early years of plastics development, most of the manufactured items were of a technical nature or were merely small parts of larger and more complex assemblies. World War II has proved to the world that plastic articles are in themselves complete entities. Shortages of vital materials, such as rubber and metal, led to inevitable substitution of specially developed plastics. In many instances the substitution was so well conceived that it is extremely doubtful whether the original material will again be used for the application. The full measure of service rendered by plastics in World War II will not be known or appreciated for some years, as many of the applications and methods still remain a secret. When the complete story is available, however, it will be found that plastics played a full-time and important part.

In a world at peace it remains for plastics to take their place with other industrial materials. Educators and designers have in the past taught the principles and techniques of metal, glass, and wood. It is now necessary for plastics to be included in these teachings. Industry must be presented with the facts about plastic

materials and techniques so that they may be applied to the fullest extent. The public must be educated to the fact that plastics do not belong in the province of black magic, but rather represent developments along the precise lines of chemistry, physics, and mathematics.

The future of the Plastics Industry is exceedingly bright. The success of this industry depends on the use of the right plastic at the right time. Plastics are definitely not miracle materials—they have their limitations and can be expected to perform functionally only within these limits. Plastics must not be applied to an item simply because the fact that it is plastic will make the item salable. The plastic must fulfil the physical and chemical requirements of the product. This is one of the major problems that will face technicians in the coming years—preventing the incorrect use of plastic materials.

It is indeed fascinating to see, for the first time, a plastic article being molded. A powder is applied between two pieces of shaped steel; it is then suddenly shut off from view, only to emerge a short time later as a bright shiny part. What happens in that "short time" is the story of this volume—the story behind the materials, the molds, and the techniques that go to make up our present-day plastics industry.

The author is deeply grateful to the following organizations for their contributions of photographs, special reports, charts, and diagrams: Agicide Laboratories, Inc.; Agricultural By-Products Laboratory; American Cyanamid Co.; American Molding Powder Co.; Arthur Colton Co.; American Society for Testing Materials; Atlas Press Co.; Becker Moore Co.; Bell Laboratories; Calco Chemical Division; Carbide and Carbon Chemicals Corp.; Catalin Corp.; Celanese Plastics Corp.; Claremont Waste Mfg. Co.; De Mattia Machine and Tool Co.; W. C. Dillon Co., Inc.; Dow Chemical Co.; E. I. du Pont de Nemours Co.; Durez Plastics and Chemicals, Inc.; Durite Plastics, Inc.; Elmes Engineering Works; Forest Products Laboratory; Formica Insulation Co.; French

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S. LEON KAYE

Metuchen, N. J.
April, 1946

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Chapter One

Development of Plastics

1-1. Plastics in Every-Day Life.—The development of plastics is a tribute to the science of chemistry. The discovery of the chemical elements involved the finding of something that already existed in nature. Plastic materials are not found as such in nature, and owe their existence to research and experiment on the part of the chemist.

It is very probable that most people have daily contact with different articles made of plastic materials without recognizing them as such. In every-day life there are many thousands of applications of plastics. Radio cabinets, knife and fork handles, buttons and buckles, shaving-brush handles, and automobile dash knobs are only a few of them.

Just as various makes of automobiles, radios, and aircraft are recognizable by name because of certain distinguishing features that the manufacturer has incorporated, so plastic materials have distinguishing marks and properties by which they may be identified. Every industry seems to possess its own language, the mastery of which is necessary to a complete comprehension of the workings of that industry. The plastics industry is no exception. Therefore, careful attention should be given to the definitions and technical terms of the plastics industry so as to become thoroughly familiar with them. Common or trade names for the various plastics should be associated with their chemical names wherever possible. For convenience, a glossary of terms used in the plastics industry is given at the back of this book.

1-2. Definition of Plastics.—The word *plastic* is derived from the Greek, *plastikos*, meaning *fit for molding*. With the growth and the development of the plastics industry, such a narrow definition cannot be considered satisfactory. While it is true that a large part of the plastics industry is devoted to the forming of articles by use of molds, this industry has invaded other fields. Plastic materials are used in the paint and lacquer industry. Synthetic fibers, such as nylon and rayon, and laminated board depend

almost wholly on their use. In the true sense of the word, none of these applications involve molding; therefore, a definition of plastics that is broad enough to include these operations is needed. Primarily, any material that will flow under the application of heat or pressure or a combination of the two is a plastic. This definition includes glass, which may be considered a plastic. The glass industry, however, has been in existence for such a long time that it is generally classed as a separate industry.

In popular usage, the word *plastic* denotes a puttylike substance, or one that, according to the dictionary definition, is "capable of being formed, or molded." A plastic material or article, in this sense, is one that is moldable. However, the development of the plastics industry has given rise to the application of the words *plastic* and *plastics* to articles that are distinctly not puttylike, or moldable; in fact, most of the items familiarly known as plastics are rigid. The reason for this use of the word is that the basic material of which these articles are made was moldable, or pliable, during the period of manufacture. Hence, the current application of these terms to the products of the plastics industry is considered justifiable, notwithstanding the fact that through chemical or physical action these products have been made rigid, infusible, and insoluble.

1-3. Scope of Plastics Industry.—Plastics is America's fastest-growing industry. During the period from 1935 to 1940, the plastics industry doubled itself in value. In order to appreciate this growth fully it is necessary to have a general knowledge of the scope of the industry, the number of plastics establishments, and the value and amounts of materials and machinery in use.

The chronological rate of growth of the plastics industry, based on plant expansion, is shown in Fig. 1-1. In about 1910, plastics first became known to the trade. The rise of the curve in Fig. 1-1 is gradual until 1931. At that time, the expansion rate shows a sharp upward trend, which continued until 1940, where even a more marked increase is noted. It is estimated that about 300 plants came into operation between 1935 and 1940. The reason for this unusual growth can no doubt be attributed to three things, namely, the interest of people in plastics, the development of new and better plastic materials, and new and more efficient machinery for the handling of materials.

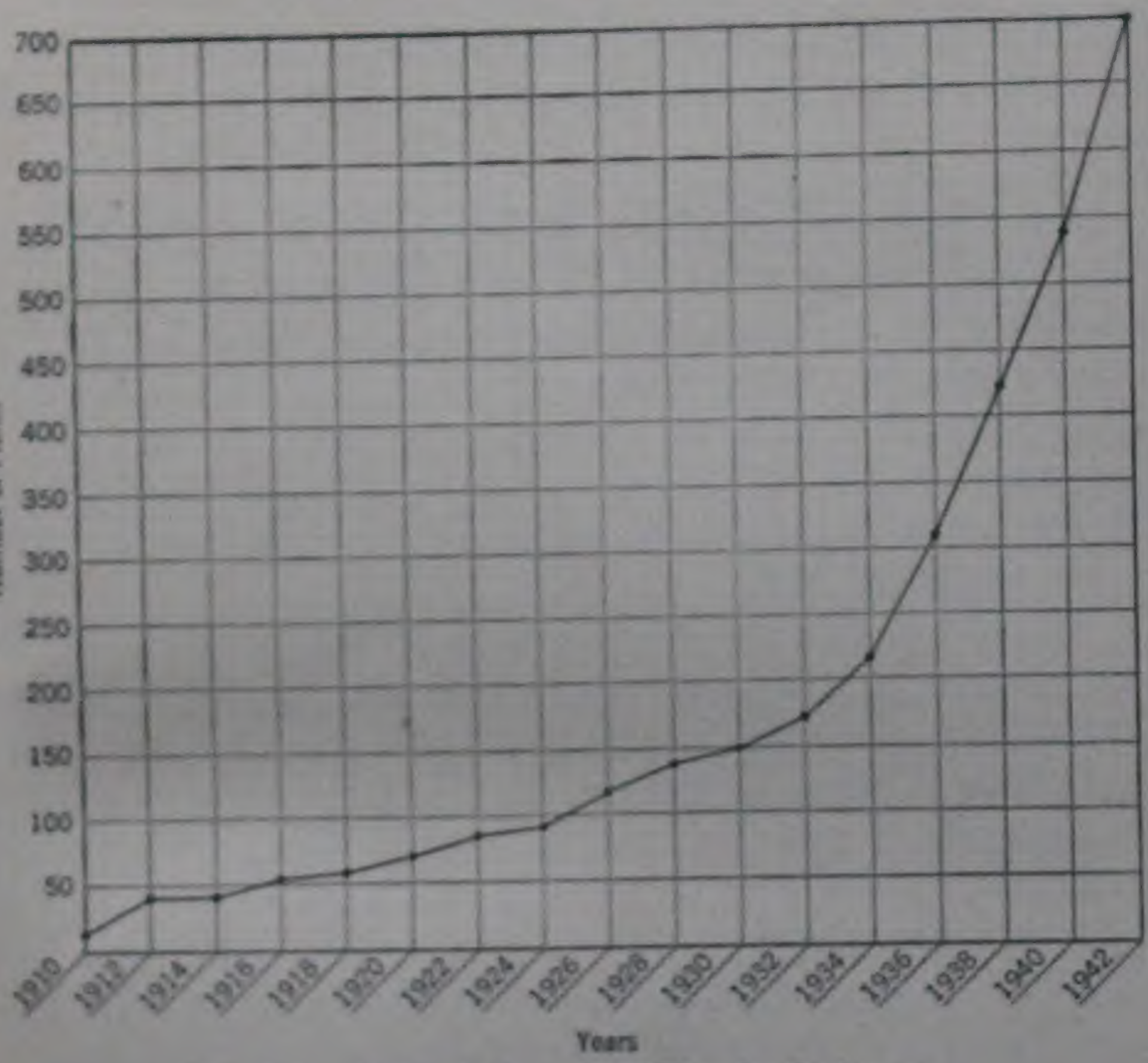


Fig. 1-1. Rate of Growth of Plastics Industry.

In 1939, the value of raw materials produced was over $63,000,000. The value of the products made from these raw materials was over $100,000,000. Although an accurate count of the many different products that make up this large value has never been made, it can safely be said that the number is over 100,000. As with other industries, various finishing operations are required on many plastic articles. In addition, numerous inserts and inlays are used. Taken collectively, the several operations require a huge expenditure of capital.

Plastic articles and materials have become an integral part of practically every industry in America. The automotive industry is one of the largest volume users of plastics. Others are the communications industry (radio, telephone, television) and the electrical-goods industry. Chain-store novelties made of plastic materials are well known to the buying public. More recently, the furniture industry, the sporting-goods industry, and the building industry have turned toward using greater amounts of these new synthetic materials. Past experience justifies the belief that

it will not be long before the use of plastics in the aircraft industry will equal, if not surpass, the volume used in the automotive industry.

1-4. Chronological Order of Development of Plastic Materials.—The first plastic, which was the material having the chemical name cellulose nitrate, came into being in 1870. The second plastic in chronological order is shellac. This is one of the oldest of all the natural substances known, but the first recorded plastic application of shellac was made in 1895. The third plastic—and the last one originally found in nature—was bitumen, which was developed in 1909.

The era of modern plastics started in 1912, when the first synthetic plastic was produced. In that year, a phenol-formaldehyde product was manufactured; and this was the forerunner of other types of phenolic plastics, as this general group is called. The next plastic material came into use in the United States in 1919 and was casein, which is a protein substance. Between 1919 and 1928, seven new plastic compounds made their appearance. Their names and the order of their invention are shown in Table 1-1.

TABLE 1-1

PLASTICS DEVELOPED BETWEEN 1919 AND 1928

Year	Material
1919	Coumarone-indene resin
1924	Cellophane
1926	Alkyd resins
1927	Cellulose acetate
1928	P enol casting resins
1928	Urea-formaldehyde resins
1928	Vinyl ester resins

In 1930 styrene was produced commercially in America, and in 1931 acrylic resins were utilized for plastics. Then improvements over cellulose acetate were obtained in the advent of cellulose acetate butyrate and ethyl cellulose. The next group of plastics includes vinylidene chloride, melamine, lignin, and vinyl resins. Bagasse, which is waste material taken from cane-sugar mills, was the next substance considered as a possible plastic. Then, Columbia resins were developed; and experiments were made on agricultural wastes such as wheat stalks, flax shives, and peanut shells.

In order to make the list of plastic materials complete, it is necessary to include glass, textile fibres, synthetic rubber, and several protective coatings.

Progress in any production field is usually measured by comparative methods of manufacture and comparative costs of articles from year to year. When a new article of manufacture makes its initial appearance, progress has been made. When the same article is made from a new material at a lower cost, further progress has taken place. It is only natural, then, that in the development of plastics each material should, in some way, be superior to those which preceded it. In this chapter, no attempt is made to list improvements in the physical and chemical properties of products in which the various plastic materials are used. The plastic materials are discussed briefly in the order of their discovery, to give an idea of the development of the plastic industry. It should be accepted as a fact that each subsequent development represents some form of progress. The plastics and their properties will be described fully in later chapters.

1-5. Cellulose Nitrate.—Credit for the invention of cellulose nitrate is usually given to John Wesley Hyatt, a printer's apprentice. As a result of a shortage of ivory in 1860, a New York firm offered a prize of $10,000 for a suitable substitute for ivory in billiard balls. Hyatt knew of this offer, and, in his effort to win that prize, the United States had its start in the plastics industry. Young Hyatt suffered the usual sore thumb from setting type. When he went to the medicine chest to obtain some collodion (a mixture of ethyl alcohol, guncotton, and ether), he found the bottle uncorked and the contents spilled over the shelf. Instead of being a liquid, it had formed a hard, solid skin. Hyatt thought that such a compound, if treated properly, could be used as a substitute for ivory in billiard balls. With his brother Isaiah, he worked with this material, in which they incorporated camphor.

The result of the efforts of the Hyatts was the first plastic molding compound. They coined the trade name, *celluloid*, which has become so familiar. Whether the Hyatts actually received the prize of $10,000 is not known, but certainly the industry which they founded brought far more to them than $10,000. A company was organized about 1872 at Newark, New Jersey, to manufacture material of this kind. The successor of that company, the Celanese

Plastics Corporation, still occupies the original site, but many new and improved materials are being manufactured.

1-6. Early Uses of Cellulose Nitrate.—One of the early uses of cellulose nitrate was in the making of collars and cuffs. Also, one of the first non-shatterable windshields on automobiles was made by cementing a sheet of celluloid between two layers of glass. It was soon found, however, that heat and exposure to ultra-violet light caused yellowing and deterioration of celluloid. Although the material now used for non-shatterable glass is of a different type, cellulose nitrate was the forerunner of the use of safety glass in the automotive industry. Large quantities of cellulose nitrate also found their way into the motion-picture industry. Another distinct use for cellulose nitrate was discovered when it was found that this material dissolved in certain solvents to produce excellent lacquers and protective coatings.

1-7. Shellac.—The records gave Emil Berliner credit for the first application of shellac as a plastic in 1895. Yet Marco Polo introduced this material in Europe in the year 1290; and several hundred years later, Akbar, the great Indian Mogul, wrote what was probably the first treatise on shellac.

Shellac is produced from the secretion of the insect *Tachardia lacca*. The lac bug, as it is more familiarly called, is found in India and South Asia. At certain times during the year, the bug settles on softwood trees, and, once established, inserts its needle-like stinger into the bast wood which lies under the bark. The sap of the tree is absorbed through this stinger, or tube, into the body, and the insect literally eats itself to death. During this gorging period the female of the species lays its eggs. A chemical process meanwhile is going on within the insect, and the liquid sap is exuded through the pores of its body in the form of a gum. The gum covers not only the eggs but also the bug. On contact with the air, the gum hardens; and the insect, caught under the gum, becomes increasingly inactive until it finally dies. Months later, the young are born. These break through the hardened shell and migrate to other trees to repeat the process. The hard crust of dark, reddish-brown material that is left on the tree is gathered and constitutes what is known as crude shellac.

1-8. Uses of Shellac.—The first commercial application in which shellac was used as a basic ingredient was the phonograph

record, and even today the manufacture of phonograph records represents the largest single use of shellac in the plastics industry. Plastics from this material find good use in the electrical field because of its excellent arc resistance, or resistance to the passage of electric current. Refined shellac, when dissolved in certain solvents, becomes the familiar shellac used for protective coverings. A more recent development is the use of shellac as a binder in the hat and paper industry.

1-9. **Bitumen.**—The third plastic to be developed came in 1909, when Emil Hemming developed a bituminous plastic. Compounds of this nature are more often referred to as *cold molded* because of the particular way in which they are handled. The importance of this material lies in the fact that for the first time in the industry an asphalt base was used in manufacturing a plastic compound. In the early days, the main use of this type of plastic was for electrical devices. In time it was found that bituminous compounds possessed better heat resistance than cellulose nitrate or shellac plastics. Consequently, handles and knobs on cooking utensils were made from it. In the last few years, the only real use has been for storage-battery boxes.

1-10. **Phenolic Plastics.**—The use of cellulose nitrate, shellac, and bitumen represents the first stage of the plastics industry. These plastics were substances originally found in nature but improved by man, mainly by mechanical processes with the assistance of some chemical treatment. The first synthetic plastic was produced in 1912, when Doctor Leo H. Baekeland produced a phenol-formaldehyde product. The Baekeland patent, issued in 1909, stated in principle that a resinous material which would harden on the application of heat could be produced if certain quantities of phenol and formaldehyde were mixed with an alkali, such as ammonia. The ammonia was not to exceed 20 per cent of the total mixture. The trade name *bakelite* has since been associated with compounds produced under that patent.

In 1911, Lawrence Redman did some work on similar compounds at the University of Pittsburgh. This work was continued under his direction at the Mellon Institute through 1913. The result was a plastic material called Redmanol after its founder. In 1922, Doctor Baekeland's corporation and the Redmanol Company merged with the Condensite Company, the latter having been

formed in 1910 to investigate materials of the phenol-formaldehyde type. The result of this triple merger was the Bakelite Corporation. In 1939, the Bakelite Corporation became a unit of the Union Carbide and Carbon Corporation.

In 1926, when the Baekeland patent expired, there was a tremendous influx to the plastics field. Such names as Durez Plastics & Chemicals, Inc., Makalot Corporation, Monsanto Chemical Co., and Reilly Tar & Chemical Corporation became familiar, and many smaller plastics molding companies began to manufacture phenolic plastics. It goes without saying that many new developments appeared during the interval between 1909 and 1926. Probably the most important contribution was made by E. E. Novotny, of Durite Plastics, Inc., who used furfuraldehyde instead of formaldehyde in his manufacturing process. Materials of this type have been on the market since 1922.

1-11. Uses of Phenolic Plastics.—Owing to their superior properties, the phenolic types of plastics found many thousands of every-day applications. The communications and automotive industries endorsed these materials almost immediately. Developments for use in the aircraft industry naturally followed. Today, phenolic plastics are, on a pound-for-pound basis, used more than any other plastic.

1-12. Casein.—Casein is a plastic produced from sour milk. It is important in the chronological development of plastics in that it is a protein substance. None of the natural substances previously used, namely, cellulose, shellac, and bitumen, was in the protein category.

Used in the form of plastic material, casein made its first appearance in Europe in about 1900, but it did not come into use in the United States until 1919; its development in this country was, no doubt, delayed by World War I and by the complex European patent situation. Christensen was probably the first to do any work on casein in the United States, his original product being known as Aladdinite.

As a plastic material, casein had an auspicious beginning. But, owing to its hygroscopicity (water-absorbent property), it lost much of its favor. A great deal of research was devoted to the overcoming of this defect but, in the meantime, new plastic materials that were superior to casein for the same applications were

developed. The advocates of the protein-type material were not discouraged, however, and as a result a plastic material derived from the soy bean was obtained. Work on zein (an alcohol-soluble protein constituent of corn) is being conducted by the Northern Research Laboratory in Peoria, Illinois.

1-13. Plastics Developed Between 1919 and 1928.—In 1919 there were only five plastic materials serving industry, namely, cellulose nitrate, shellac, bitumen, phenol formaldehyde, and casein. Although all five are still being used, only the phenolic type has continued to progress toward newer and better materials. It required 49 years to produce five plastics; yet from 1919 to 1940 almost three times that number were produced. This progress reflects the interest of the buying public. The seven plastics developed between 1919 and 1928 are listed in Table 1-1 on page 4. In the order of their invention, they are coumarone-indene resin, cellophane, alkyd resins, cellulose acetate, phenol casting resins, urea-formaldehyde resins, and vinyl ester resins. All these products except the phenol casting resins seem to have been developed for allied fields. For example, the coumarone-indene resins were developed as an adhesive and protective coating for the paint and lacquer industry. This is also true of the alkyd and vinyl ester resins. Cellophane was naturally applied as a protective coating in the packaging field.

Phenolic casting resins came as an outgrowth of Baekeland's original research in 1912, but, instead of the resin being formed as a thick, syrupy mass, it was poured into shapes. In this way, a crude article was formed. This was a direct development in the plastics industry. It is significant, however, that in almost every case these developments were directly applied to the production of plastic compounds.

1-14. Urea Plastics.—Although patents on urea materials were granted as early as 1920, it was not until 1929 that a usable urea plastic, known as urea-formaldehyde molding compound, made its first appearance. Most of the earlier commercial compounds were unsatisfactory because of their instability. Research by Carleton Ellis showed that this defect could be remedied by the addition of a filler, such as wood pulp. The pioneer work on urea plastics was conducted by the American Cyanamid Company in conjunction with Toledo Synthetic Products, Inc., and it was

through the efforts of these two companies that urea attained recognition in the plastics industry.

The Toledo Scale Company had been searching for some time for a suitable material to house its scales, and this search led to the development of urea plastics. The white material resulting from the experiments carried on at the Mellon Institute, where a project had been set up, was urea-formaldehyde molding compound. In many respects, the urea-formaldehyde compounds are identical with the phenolic-formaldehyde compounds, the most noticeable difference being their relative receptivity to colors. The phenolic materials were limited, for various chemical reasons, to the darker shades, whereas the urea materials could be produced in pastel shades. The eye appeal of urea plastics caused them to enjoy immediate public acceptance.

1-15. Cellulose Acetate.—From the time of its inception, the fire hazard of cellulose nitrate was recognized, and the development of cellulose acetate probably resulted from the search to find a less inflammable material. The patent situation for the development of this material is complicated. Suffice it to say that work had been done on cellulose acetate as early as 1894, but, according to Table 1-1, this material was not developed until 1927. In that year it was available only in sheets, rods, and tubes, in which forms it is comparable to phenolic casting resins. Other early uses were as artificial silk and as "dope," that is, as a base in lacquers. The actual commercial career of cellulose acetate, however, started with its use as a molding powder in 1929. After that time, it took its place quickly with the other plastic materials and soon ranked second, in quantity consumed, to the phenolics.

1-16. Styrene Plastics.—The story of styrene in the plastics field is a peculiar one. The resin was known as early as 1831; yet it was not thought of as a possible plastic until about 100 years later. In 1831 the natural styrene was extracted from a certain type of balsam. It was first produced synthetically in France in 1869, but not until 1930 did the Naugatuck Chemical Company produce it commercially in America. The compound in the first stages of production presented many difficulties and did not meet with much success, but, as a result of continued research, the Dow Chemical Company produced the first successful styrene molding compound. Owing to its clarity and its tinkling sound when struck, styrene is

sometimes referred to as synthetic organic glass. Since styrene is a completely synthetic product, whereas cellulose acetate depends on natural cellulose for its formation, the probabilities are that styrene will replace cellulose acetate as the second-ranking plastics compound in quantity consumed.

1-17. Acrylic Resins.—The acrylic-acid resins have been known for a long time, but it was not until 1931 that they were utilized for plastics. It was found that, when the resins were dissolved in suitable solvents, they were adequate as binders for laminated glass and surface coatings. Doctor Otto Röhm was directly responsible for these first researches. Further research work was done to change the chemical structure of the acrylic-acid resins to methyl-acrylic-acid resins. With this change, these resins became an important factor in plastics. Instead of being used as protective coatings, the new materials were found suitable as molding powders and were marketed as such. Owing to the remarkable optical properties of the resin, it became the leading material for gun turrets and cockpits for aircraft. Methyl-acrylate resins are more optically clear than styrene resins. The many exceptional chemical properties of methyl acrylate make it a leading material in the denture field.

1-18. Cellulose Acetate Butyrate.—A further improvement over cellulose acetate resulted when cellulose acetate butyrate was developed. Its first appearance was in the lacquer field as a protective coating. As with the acrylics, which also developed from protective coatings to molding compounds, the butyrates later appeared as molding materials. Their advantage over ordinary acetate was due to the fact that they had better form stability under heat. Cellulose acetate butyrate is sometimes called Tenite II or aceto-butyrate.

1-19. Ethyl Cellulose.—As the name indicates, ethyl-cellulose plastics depend on natural cellulose as a base, just as cellulose acetate, nitrate, and butyrate do. The cellulose, however, receives a different chemical treatment, which results in a different end-product. Ethyl cellulose first appeared as a protective coating. Research by Hercules Powder Company and Dow Chemical Company resulted in the formation of a molding compound. Many of the disadvantages of the allied cellulose compounds were sur-

mounted by ethyl cellulose. The standard practice in the plastics industry is to use cellulose acetate wherever the application calls for a cellulose product. Where special features are required, such as heat and moisture resistance, ethyl cellulose or cellulose acetobutyrate is used.

1-20. Vinylidene Chloride.—The Dow Chemical Company, through an extensive research program, produced vinylidene chloride. Its particular claim to fame, other than a few superior properties, was that it could be produced in a flexible form. In the electrical industry it found almost immediate use as a coating for wire, and later it appeared as the flexible-coil hosing on various machines.

1-21. Melamine.—The melamine compounds are to be considered in the same family as the ureas and phenolics in that the formaldehyde used in their formation is a basic raw material. Also, the physical and chemical properties of the melamine compounds are closely allied with those of the ureas and phenolics. Melamine was known as early as 1834 but its use as a plastic did not come until the American Cyanamid Company commercially marketed it in 1939.

1-22. Lignin Plastics.—Ordinary wood consists of about 50 per cent of cellulose. In addition, it contains approximately 25 per cent of a resinous substance called lignin. Lignin, when chemically activated, can be made to combine very readily with phenolic, urea, or melamine resins. The research work on lignin was mainly an endeavor to find a method of activating the material, as well as a satisfactory procedure for combining it with various other resins.

The Forest Products Laboratory, established by the United States Government, has done work on both urea-lignin and phenolic-lignin combinations. The advantage of lignin plastics is mainly from the standpoint of cost. For example, a phenolic plastic contains a certain percentage of resin mixed with other constituents, such as wood flour. By activating the lignin in the wood flour, it is possible to reduce the per cent of phenolic resin in the plastic. In certain cases, this reduction has been as much as 15 per cent. Laminated materials using lignin plastics have been on the market for some time. An example of a lignin laminate is a wallboard marketed under the name of Masonite.

In critical times, when essential materials such as phenol are limited, lignin plays a very important part, since its use permits an extension of the supply of critical materials.

1-23. Vinyl Resin Plastics.—There are many vinyl resin plastics. Most of them at some stage in their development served the paint industry as lacquer bases. The full usage of the vinyls is not known, as the compounds are too new. However, much more information is available concerning these compounds in connection with synthetic rubber and textile fibers.

1-24. Bagasse.—Investigation of bagasse, a waste material from cane-sugar mills, as a possibility for plastics had its inception at the Agricultural By-Products Laboratory at Ames, Iowa. Little is known at the present time as to the status of bagasse plastics. However, the utilization of any waste product to form a usable material has worth-while potentialities.

1-25. Columbia Resins.—Not much information is available regarding the Columbia resins, other than that they are completely synthetic resins developed by the Pittsburgh Plate Glass Company. At present, they appear as cast sheets, but work is under way to produce a molding powder. The optical properties of resins of this type are said to be superior to those of the acrylics.

1-26. Agricultural-Waste Plastics.—The United States Government set up four regional laboratories to experiment on various waste products to be utilized in industry. The Northern Regional Research Laboratory was the one assigned to plastics from agricultural wastes. Through the work of Williamson and Lathrop, the laboratory developed commercial plastics using wheat stalks, flax shives, and peanut shells. Like lignin, these materials are not used alone, but are employed in combination with phenolic or urea resins. With the agricultural wastes amounting to more than 100,000,000 pounds per year, the commercial success of plastics of this type is practically assured.

1-27. Other Materials Used in Plastics Industry.—Some of the materials used in the plastics industry—glass, for example—are not thought of as plastics. They are definitely of a plastic nature; yet they are basic materials in industries, such as the glass industry, that are large enough in their own right to be known as

something other than merely a part of the plastics industry. Other conspicuous examples are various textile fibers, rubber, and protective coatings.

1-28. Synthetic and Natural Yarns.—For many generations clothing was made of natural products, such as cotton, wool, and silk, but in more recent years research has provided a new group of chemical fibers. Now much clothing is made of rayon, the development of which dates back to the beginning of the twentieth century. There are many types of rayon on the market today, but the generic term *rayon* is applied to all fabrics made with cellulose as a base. The name *nylon* also is already common. It is a representative of the synthetic-fiber group and is a product of DuPont experimentation. Its applications continue to multiply. In addition to its use in wearing apparel the material soon became commercially available for bristles in tooth brushes and hair brushes. Subsequent development gave the world surgical sutures and fabrics. Among its many other applications is its use as parachute material.

1-29. Synthetic Rubber.—Rubber has long been known as the natural product of certain trees. For many years it has been the great desire of the chemist to imitate nature and synthesize rubber. That desire has at last been partially achieved, and no less than four different types of synthetic rubber, or elastomers, are being produced. As with glass and textiles, the rubber industry is far too large to be classed as a subsidiary industry of plastics. However, no study of plastics is complete without the knowledge of these synthetic rubber compounds.

1-30. Protective Coatings.—While a number of materials of a protective-coating nature have been mentioned as plastics, it is more logical to class them as part of the allied paint and lacquer industry. One of the largest classes of plastic materials in this category comprises the alkyd resins. Lacquers in which this resin is used as a base have found great popularity as automobile finishes, owing to the ease of application and the short drying period.

Another well-known class of materials in the lacquer field comprises the urea-formaldehyde coatings. These lacquers are formed by dissolving the urea-formaldehyde resin in suitable combinations of alcohols and esters. The peculiar property of this type

of finish is that it hardens by an application of heat rather than by oxidation. Many of the late-model cooking ranges and refrigerators are finished with a urea-formaldehyde material. Phenol-formaldehyde resin is being used in the same manner, although it is limited to darker colors.

Cellulose lacquers, commonly referred to as "dope," have been known for a long time. Dope is probably used for aircraft fabric finishes more than any other lacquer. Cellulose nitrate, acetate, and butyrate, as well as ethyl cellulose, all serve as a base for lacquers grouped as cellulose finishes.

Vinyl resins are adaptable as synthetic finishes, although their use is confined mostly to special purposes. The linings of metal tanks and beer cans are examples. Vinylidene chloride that is made as a molding compound for flexible articles is used also as a lacquer base, and the resulting product makes an excellent cable lacquer, as it does not lose its flexibility even at extreme temperatures.

The acrylic resins show great promise for use as lacquers. Probably one of the most difficult substances to coat is leather; yet the acrylics prove very satisfactory for this purpose. Many of the high-gloss artificial leathers on the market today owe their appearance to a coating of acrylic lacquer. This lacquer possesses the property of permeating the leather and becoming an integral part of it.

Chapter Two

Basic Principles of Manufacture

2-1. Primary Classes of Plastics.—All plastic materials are placed in two general groups, namely, thermosetting materials and thermoplastic materials. A thermosetting material is one which achieves its rigidity through a chemical reaction. Plaster of Paris is a good example to illustrate the meaning of a thermosetting material, although it is not classed as a plastic material. Powdered plaster of Paris and water are mixed together to form a viscous, dough-like mixture, which is poured into a mold, or shape. Within a short time it will be found that a chemical change has taken place and that the mass has cured, or has become hard. If the hardened material were ground into powder and water were added, it would be found that the process of forming a viscous mixture and curing would not repeat itself. The plaster of Paris, having once undergone a chemical reaction, is no longer fit to be used for the same purpose again. The same thing occurs when a thermosetting material is used. *Once a thermosetting material has undergone a chemical change, through the media of heat and pressure, it cannot be used again for the same operation.* The word *thermosetting* is derived from *therme*, meaning *heat*, and *setting*, meaning *hardening*. Hence, the word means *hardening under heat.*

Unlike thermosetting materials, thermoplastic substances undergo a physical change only. A bar of milk chocolate serves as an example. When heat is applied to the chocolate, it melts and can be poured into a form, or mold, such as an ice-cube tray in a refrigerator. When cooled and hardened, the chocolate will have taken the shape of a cube. The cube can now be melted and transformed into the original candy bar. Throughout the physical changes, the chemical constitution of the chocolate has remained the same. Therefore, when using a thermoplastic material, it is necessary to supply some means of cooling the softened material.

The division of materials into thermosets and thermoplasts is a natural one in almost every case. Some versatile materials, called *borderline compounds*, seem to fall into both classes. In the study of such compounds, it will be found that conditions of acidity or

alkalinity, and of heat and pressure, will in any one case make the material either thermoplastic or thermosetting. There cannot be a material which is heat-setting and cold-setting at the same time.

2-2. **Secondary Classes of Plastics.**—In conjunction with the two generic classes of plastics, there are four subdivisions. Each plastic material must represent one of the divisions, which are as follows: synthetic resin, cellulose derivative, protein, and natural resin.

TABLE 2-1
CLASSIFICATION OF MOLDING MATERIALS

Thermosetting Compounds	Thermoplastic Compounds	Borderline Compounds
Phenol formaldehyde (S)	Shellac (N)	Bitumen (N-S)
Phenol furfural (S)	Cellulose nitrate (C)	Casein (P)
Urea formaldehyde (S)	Cellulose acetate (C)	
Cast phenolic (S)	Styrene (S)	
Melamine (S)	Acrylic resins (S)	
Lignin (S-C)	Vinylidene chloride (S)	
Bagasse (S-C)	Ethyl cellulose (C)	
Columbia resins (S)	Cellulose acetate butyrate (C)	
Agricultural wastes (S)	Vinyl resins (S)	

S—Synthetic resin; C—Cellulose derivative; N—Natural resin; P—Protein.

A synthetic resin may be defined as a complex organic material made by the chemical reaction of simpler substances. In most cases, the chemical reaction is a condensation reaction.

A cellulose derivative may be defined as any material made from or with cellulose as a base.

The protein compounds are limited to those plastics which are made with some protein as a base. A protein in itself is an organic compound composed of carbon, hydrogen, oxygen, nitrogen, and sulfur.

The natural resins are described as exudations from various plants and animals.

The classification of the plastic molding compounds in use today is shown in Table 2-1. An examination of the thermosetting group indicates that all such materials are in the synthetic-resin category, although two of them are also cellulose derivatives. The thermoplastic group includes all categories except the protein. The borderline group consists of protein compounds and natural and synthetic resins.

In commercial practice, casein compounds are treated as thermoplastic materials in the formation of the molded articles. Subsequent chemical treatment transforms casein to the thermo-setting class. Bitumen is commercially treated as a thermoplastic compound in its initial stages. However, with the subsequent application of heat, the material is converted to the thermosetting class.

In general, thermosetting and thermoplastic compounds each require a distinct type of molding procedure. Without going into specific details of molding, a thermosetting material generally is handled by placing it in an open mold and then closing the mold. Subsequent addition of heat and pressure for a specified length of time will result, on opening the mold, in a plastic molded article. A thermoplastic material generally is handled by forcing a heated charge of material into the closed mold. A subsequent cooling to below the softening point of the material results, on opening the mold, in a molded article.

2-3. Condensation.—A definite chemical reaction in which two or more like or unlike molecules combine with the loss of water or gas is known as condensation. Resins are formed by condensation reactions, but all condensation reactions do not produce resins. However, in the terminology of the plastics industry, the word *condensation* is usually restricted to those reactions from which a resinous material is formed as the main product.

Resins were formerly the chemist's curse. In many cases, when chemicals were mixed and heated, the by-product became a tarry mass in the bottom of the flask. When it became evident that these gummy substances had commercial possibilities, research was started on them. It was found that, by controlling the heat during the reaction, the nature of the resinous mass could be controlled. It was also discovered that two substances react differently in an alkaline medium than in an acid medium. Furthermore, it was found that the gummy mass was produced when the reaction was allowed to proceed beyond the condensation stage. For practical purposes, it was desirable to stop the reaction when the original condensation was complete. By close study, it was shown that there was a definite demarcation between the condensation and the next stage.

After condensation is complete, there is noticeable a distinct separation between the resin and the water, and, before the former can be commercially adapted, the water must be removed. In certain rare cases, the by-product is a gas. The gases in these reactions are carried off while the reaction is taking place.

Many raw materials when mixed with each other show no disposition toward reacting. It then becomes necessary to add a catalyst to promote the reaction. Although a catalyst takes no part in the reaction, it definitely has a directive influence on the outcome.

2-4. Polymerization.—The linking together of similar molecules to form one large molecule, or macromolecule, is known as polymerization. It is the stage of reaction that follows condensation. The resin formed in the condensation reaction, known as the monomer, is not, as such, suitable as a molding material, but is used as the base for lacquers. The chemist's job is to convert the monomer into the polymer. By subjecting the monomer to various conditions of heat and pressure, the chemist found that this conversion could be made. The resin in the monomeric stage has a known molecular weight. The polymer is an unknown multiple of this weight, and is usually expressed as

$$\text{polymer} = (\text{monomer})_n$$

in which n represents an indeterminate number.

It can be expected, and properly so, that by varying the conditions of heat and pressure on the monomer the molecular weight of the resulting polymer will vary. A prolonged heating under a high temperature will produce a polymer with a large molecular weight. High pressure will cause the same result. It is common to talk of polymerized substances as having a certain polymerization. In general, the monomer is a liquid, whereas the polymer is a solid. Synthetic resins are usually amorphous and therefore have no definite melting point. However, there is a definite temperature range in which they soften. Since the transformation from the monomer to the polymer is the change from a liquid to a solid, there is a change in viscosity during the process. Likewise, as the viscosity increases, the temperature at which the material begins to soften increases. It then follows that, as the degree of polymerization is extended, the hardness of the compound increases. There

are definite limits, however, to hardness as far as practicability of molding is concerned. The same is true of softness.

2-5. Polymerization of Synthetic Resins.—Only synthetic resins undergo polymerization. It might seem somewhat strange that synthetic resins are found in both thermoplastic and thermosetting types of molding compounds. This may be explained by the fact that a synthetic resin in the thermoplastic category is very highly polymerized when it is used as a molding compound, whereas a synthetic resin in a thermosetting molding material is only partially polymerized. The complete polymerization occurs in the actual molding operation.

Some synthetic resins are abnormal in their behavior—they polymerize almost spontaneously. In the case of a material of this type, it is sometimes necessary to slow down, or retard, the action. This is done by adding to the monomer a chemical compound known as an *inhibitor*. Such a chemical substance, or negative catalyst as it is sometimes called, is very useful, as it acts as a controlling agent for the resin manufacturer by regulating the degree of polymerization to within specified limits. On the other hand, some synthetic resins present difficulties in polymerizing. In the case of a material of this kind, it is necessary to add a positive catalyst to encourage polymerization.

The purity of the raw chemicals used has a distinct bearing on polymerization. In some cases, impurities will act catalytically to cause spontaneous polymerization, and in other cases they are just as liable to act as inhibitors to prevent polymerization. Although synthetic resins of the polymerizable type have been manufactured since 1921, they still present many production problems. For this reason, the manufacturer of resins of this type must spend many thousands of dollars on testing equipment and on temperature and pressure controls. It is of prime importance that the chemical composition of all the raw materials be well known. It is equally important to control the temperature and pressure during the reaction.

2-6. Basic Ingredients of Plastic Molding Compounds.—A plastic material, although it is thought of as a single entity, is made up of several component substances. Every plastic molding compound is composed of the following basic materials: binder

(base), filler, coloring matter, lubricant, accelerator or inhibitor, and plasticizer.

The binder, or base, of every plastic, whether thermoplastic or thermosetting, falls into one of the following four categories: synthetic resin, cellulose derivative, natural resin, or protein. The per cent of binder in a compound will vary with the kind of plastic to be produced. The binder is the most important ingredient in the molding compound, as its function is to bind the other ingredients to one another so as to hold the compound together.

The filler is the ingredient that imparts the various physical properties to a compound. The per cent of filler will vary in different compounds. A great variety of fillers are in current use. If a high-impact material is required, the filler would probably be macerated rag. Heat-resistant compounds contain asbestos as a filler.

Pigments or dyestuffs are added to plastics to impart color. The amount of coloring matter in any compound is determined by the strength of the coloring matter itself and also by the chemical action, if any, of the resin on the dyestuff. For example, phenolic molding compounds are not usually found in pastel colors, because phenol has a destructive action on most light-color dyestuffs. Phenol turns yellow on aging and this discoloration interferes with the effects of pigments that may have been used as coloring matter.

In the fabrication and use of molding compounds, it is necessary to prevent the plastic from sticking to the manufacturing apparatus or to the molds which give the plastic articles the desired shapes. For this purpose a lubricant is used. Lubricants are usually waxes that decompose only at very high temperatures. Too much lubricant in a compound will cause scumming on the surface of the molded article. To overcome this difficulty, two lubricants are oftentimes used. One has a low melting point so that it volatilizes during the material-manufacture process; the other lubricant, which has a higher melting point, remains in the compound and serves its purpose in the molding operation. The per cent of lubricant in any compound will depend to a great extent on the shape of the molded article for which it is to be used.

In plastics of the thermosetting type, it is usually necessary to adjust the state of polymerization of the binder (resin). The resin may be either too advanced (polymerized too far) or not advanced far enough. The adjustment is made by the addition of

either an accelerator or an inhibitor, as the need dictates. An accelerator chemically activates the resin so that subsequent operations will bring the resin to the desired polymerized state. The inhibitor, or retarder, acts in just the opposite manner. It holds back, or slows up, the rate of polymerization. The per cent of the accelerator or inhibitor depends entirely on the polymerized state of the resin as it is being converted into a molding compound.

The plasticizer in the molding compound is the ingredient which is responsible for the characteristic of flow. Flow can best be explained by the following illustration: Two compounds are identical with the exception of the plasticizer. One has a plasticizer, and the other does not. Under the same conditions of temperature and pressure in molding, the compound with the plasticizer will be easier to move and it will move through a greater distance. When used with a thermoplastic material, a plasticizer also imparts some physical and chemical properties. The per cent of plasticizer in a compound will depend to a great extent on the intricacy of design of the article to be molded. The method of molding also determines the amount of plasticizer to be used.

2-7. Apparent Omission of Some Ingredients.—All six of the essential basic ingredients are found in every plastic compound, but in some cases two of the six are embodied in one chemical material. This combination is found mostly in thermoplastic materials. For example, the resin might be slippery by nature. It is entirely plausible, then, that no lubricant will be needed. Again, the mold might be chromium-plated to lower the friction, chromium being a metal that is slippery. The slipperiness of the chromium plating then serves the same purpose as a lubricant. Similarly, if a crystal-clear, transparent material is required for an application, no coloring matter would have to be added. Therefore, the resin acts as both the binder and the coloring matter. In the case of plastics of the cellulose-derivative type, the binder and the filler are embodied in the one material—cellulose. In many cases, the plasticizer and the lubricant are represented by a single substance.

Although a plastic molding compound always consists of six basic ingredients, any one compound might have to have only five or four. In such a case, it will be found that one substance is

fulfilling the functions of two of the basic six components; or each of two substances serves a dual purpose.

2-8. Cure.—The term *cure* is applied only to thermosetting molding compounds. When a molding compound of the thermosetting type is used to make a plastic article, it is important to know how much time is required for the molding compound to become rigid in the mold, or for how long the material must be cured. Cure is a very important factor to a molder, as it represents time; and most molders base a good part of the manufacturing cost of an article on the time required to produce it. When a thermosetting compound changes from its initial state of fusibility and solubility to one of infusibility and insolubility, it is not the filler, lubricant, plasticizer, dyestuff, accelerator, or retardant that goes through this change. It is the binder, or the synthetic resin. The accelerator or inhibitor will either hasten or retard this change, as the case may be. The rate of cure depends on several factors, among which are the condition of the resin and the wall thickness of the article to be produced.

2-9. Pressure Time.—Where thermoplastic materials are concerned, there is no such thing as cure in the sense that the material goes from the soluble stage to the insoluble stage. Thermoplastic materials undergo a physical change only. In the production of a plastic dish from a thermoplastic material, the question arises as to how long the material must be kept in the mold before rigidity of the plastic is achieved. The answer lies in the time required to bring the temperature of the material below its softening point. In speaking of a thermoplastic material, the term *pressure time* corresponds to the word *cure* as related to a thermosetting material.

2-10. Correlation of Flow and Cure.—A definite correlation exists between flow and cure. It would not be economical, in the production of a plastic radio cabinet, to have the material cure out, or achieve rigidity, before the material had flowed sufficiently to form a complete article. Flow, which can be measured in terms of hardness or softness, must be coordinated with the cure time of the compound. In general, the softer the flow, the longer the cure time; the harder the flow, the shorter the cure time.

In order to achieve some degree of uniformity, there are standard tests of both flow and cure of a material. Manufacturers

of thermosetting molding materials designate the flow by numerical values so that the consumer can, in ordering his material, be assured that the flow is correct for his application.

2-11. Correlation of Flow and Pressure Time.—In the case of a thermoplastic material, there must be a correlation between flow and pressure time. The hardness or softness of a thermoplast is mainly controlled by the per cent and type of plasticizer used in the compound. Naturally, a change in the amount of plasticizer used will change the softening range of the compound. This means that there will be a change in the pressure time. For example, a molding compound has a molding temperature of 400° F. This is the practical temperature needed to make the material flow to form the article. The temperature at which the plastic begins to soften is about 260° F. The pressure time is the time required to cool the material of the formed article from 400° F to a little below 260° F. It becomes obvious that the greater the difference between the molding temperature and the temperature at the softening point, the longer the time required to achieve the cooling.

Chapter Three

Early Plastic Materials

Cellulose Nitrate

3-1. Chemistry of Cellulose Nitrate.—After many years of discussion, it is now accepted that the cellulose molecule is made up of an unknown number of glucosidic units, the structure of one of which is shown in Fig. 3-1. The cellulose molecule is large,

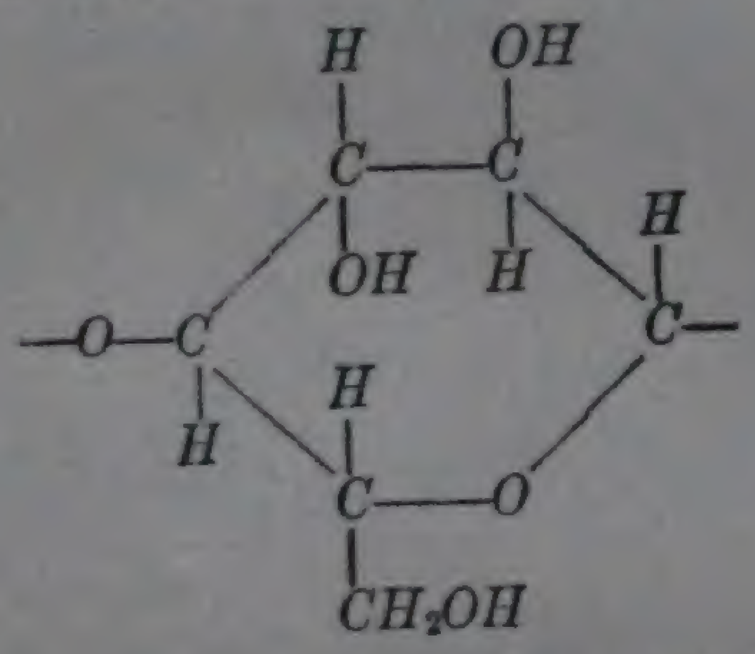


Fig. 3-1. Structure of Glucosidic Unit.

and as many as 3,000 of them can be connected together. Each molecule has three reactive hydroxyl groups. Many of the groups, in the process of nitrating cellulose, are replaced by nitrate groups. If all the hydroxyl groups were replaced by nitrate radicals, the nitrogen content would be slightly over 14 per cent. In actual practice, complete nitration is never achieved.

The degree of nitration is usually measured on the basis of the nitrogen content of the commercial material. Cellulose nitrate, used for explosives, contains about 13 per cent of nitrogen. Material used for protective coatings and photographic film has about 12 per cent. The percentage of nitrogen in compounds used for plastics runs from about 7 to 11 per cent. The rate of combustion, the solubility, and the compatibility with plasticizers will depend on the nitrogen content.

3-2. Raw Materials.—Cellulose nitrate is classified as a thermoplastic material of the cellulose-derivative type. The basic raw material used in its manufacture is cellulose, the two sources of which are pure cotton linters and wood pulp. Various research

(Courtesy of Tennessee Eastman Corp.)

Fig. 3-2. Cotton Linters for Cellulose Nitrate.

laboratories, such as the Forest Products Laboratory, are constantly at work, however, attempting to find new sources of raw materials, such as agricultural wastes. The best cellulose plastic is produced when cotton linters, shown in Fig. 3-2, are used. As these contain many impurities when gathered, they must go through a very thorough cleaning process.

Nitration of cellulose is carried out with nitric acid, which is usually produced by the catalytic oxidation of ammonia. In the manufacture of cellulose nitrate, a variety of plasticizers are used, but the most important is probably camphor, which is either produced synthetically from oil of turpentine or distilled from wood. The coloring matter consists of earth pigments and dyestuffs of the alizarin and azo types. The pigments are usually employed to make the compound translucent or opaque; the dyestuffs, to give the brilliant colors. The choice of the dyestuff is important, as it must have good resistance to sunlight. Since cellulose nitrate is a thermoplastic material, it needs neither an accelerator nor an inhibitor. The cellulose acts as both binder and filler. Owing to the nature of cellulose nitrate in the finished form, it is not essential

to use a lubricant; hence, in this respect, the plasticizer can be considered the lubricant.

3-3. Flow Chart for Manufacture.—Because of the continuous fire hazard in the production of cellulose nitrate, strict precautions are necessary. The equipment is usually designed in such a manner as to insure instantaneous dumping of materials in case of fire. In all operations where heat is either supplied or given off by a reaction, temperature-control instruments are used. In the various stages of manufacture, the material is extremely dangerous, and too much care cannot be exercised.

A flow chart for the manufacture of cellulose nitrate is shown in Fig. 3-3. This chart merely gives an over-all view of the succeeding points and processes of manufacture, the details of which are taken up in regular order in the following paragraphs. It will be helpful to refer to this chart from time to time as the details are studied.

3-4. Nitration.—The manufacture of cellulose nitrate starts with the nitration of the purified cotton linters, which have been dried to a moisture content of 1 per cent. The nitration takes place in a chrome-lined metal tank into which a mixture of three parts of sulfuric acid to one part of nitric acid has been placed. The linters are added to this mixture and are immediately submerged. Before this addition is made, however, care must be taken that a large excess of acid mixture is in the tank. There must be about 2 gallons for every pound of linters to be added. The reason for this is as follows: The combination of sulfuric and nitric acids always produces heat. This heat is more intense when the linters are introduced, and, unless an abundance of liquid is in the tank, an explosion is liable to result.

The nitration tank is jacketed so that cold water may be circulated through the jacket to insure temperature control of the mixture. The temperature and the length of time allowed for the reaction will control the degree of nitration. To obtain a nitrogen content of approximately 10 per cent requires about 30 minutes, during which time the temperature should be held below 100° F. There must be constant mechanical agitation throughout the nitrating period. At the end of this period, the cotton linters are slightly yellow and they are more brittle than before. In other respects, they appear to be unchanged.

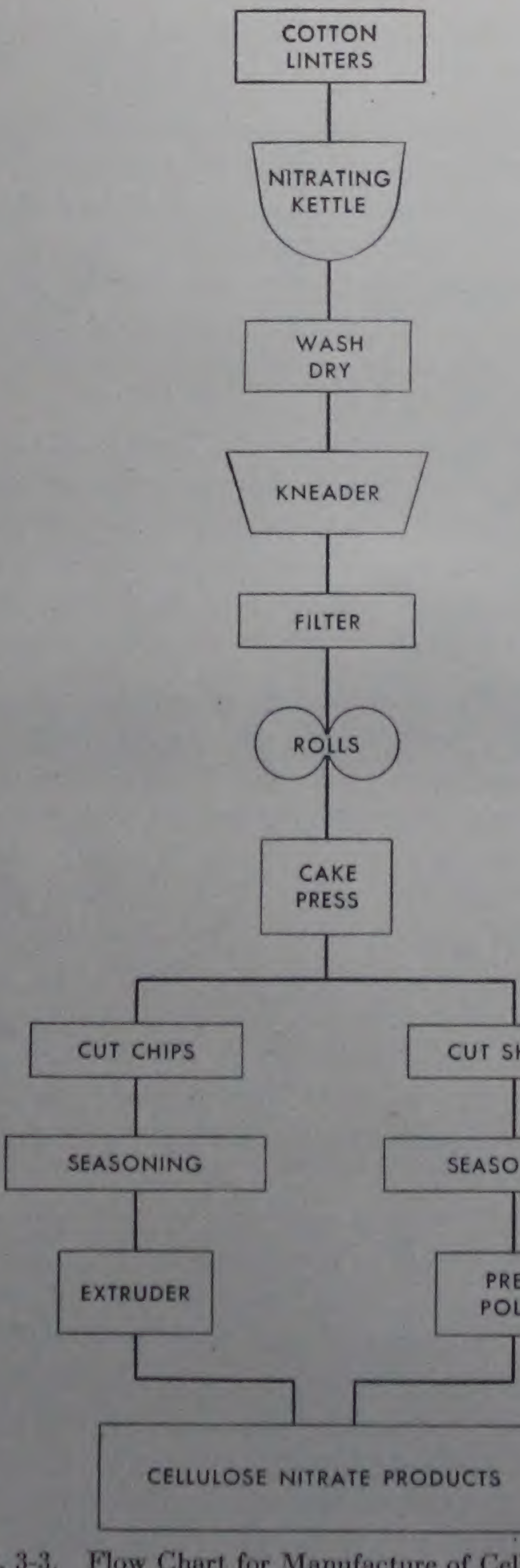


Fig. 3-3. Flow Chart for Manufacture of Cellulose Nitrate.

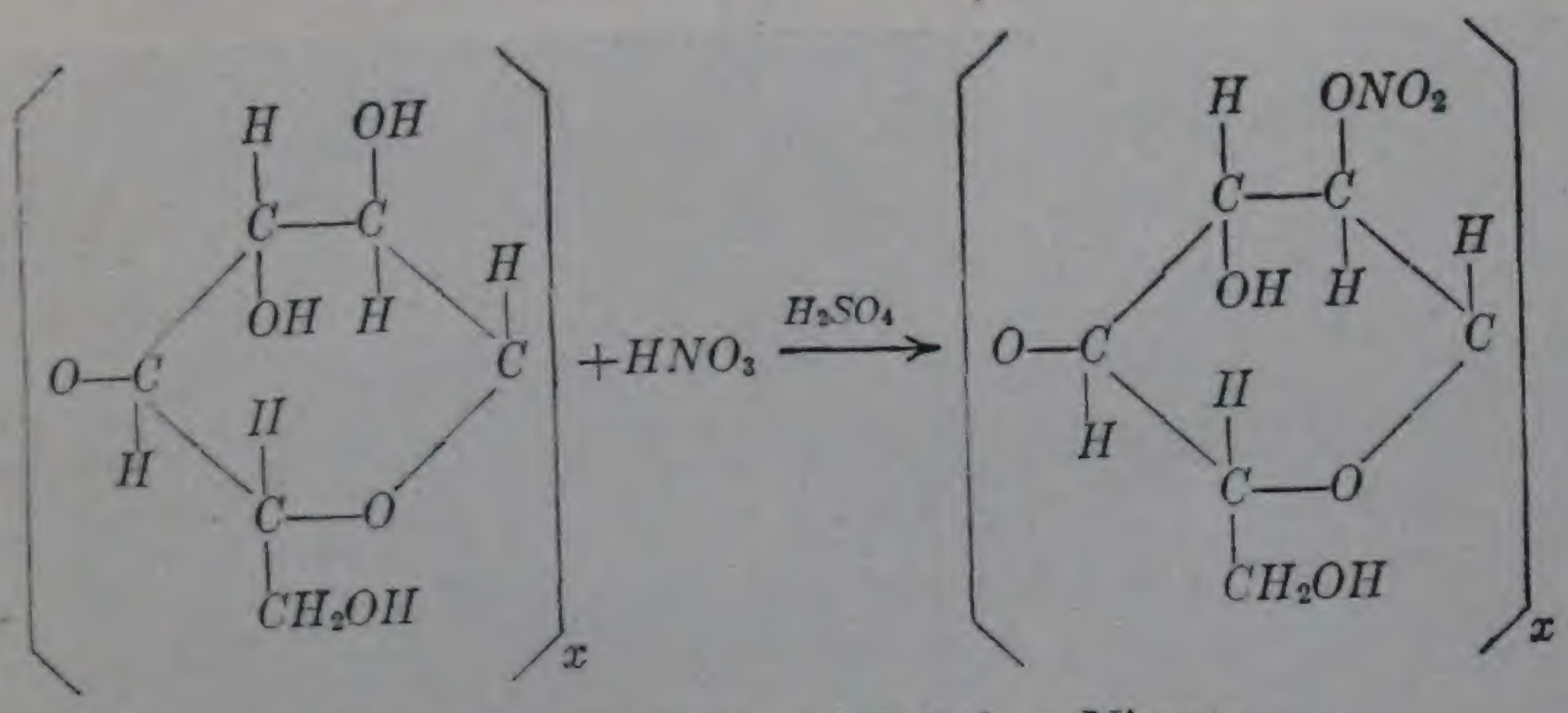


Fig. 3-4. Structure of Cellulose Nitrate.

Since each glucosidic unit has three hydroxyl groups that can be replaced by nitrate groups, the question arises as to which of the hydroxyls actually are replaced. In a chain of 1,000 of these units, there are some 3,000 hydroxyl groups, and, as the desired nitrate content is about 10 per cent, only a small fraction of the 3,000 will be replaced. The actual replacement is haphazard. Any of the hydroxyls may be acted on. In Fig. 3-4 is shown a fair representation of the structure of cellulose nitrate.

3-5. Methods of Drying.—On completion of nitration, the excess acids and water formed by the reaction are drained off. It has been found that an efficient means of removing the last traces of excess liquids is the process of centrifuging, which consists in whirling the material at high speed, the excess moisture being thrown off by centrifugal force. A centrifuge is shown in Fig. 3-5.

There are two other methods by which drying may be accomplished. The material may be put into a press, in which the moisture is squeezed out. The other method is to add alcohol, which dissolves the water. Whichever method is used, it is necessary to keep in mind that the mixture is combustible and that high temperatures must be avoided. It is usually necessary to wash the nitrated cellulose with boiling water to insure the removal of all acid. In any case, the material must be dried.

At this stage of manufacture the material is nitrocellulose. It is not suitable as a plastic because it will not readily flow under the heat and pressure required for molding operations. It is, however, suitable for the production of protective coatings. For the production of plastics it must be further processed.

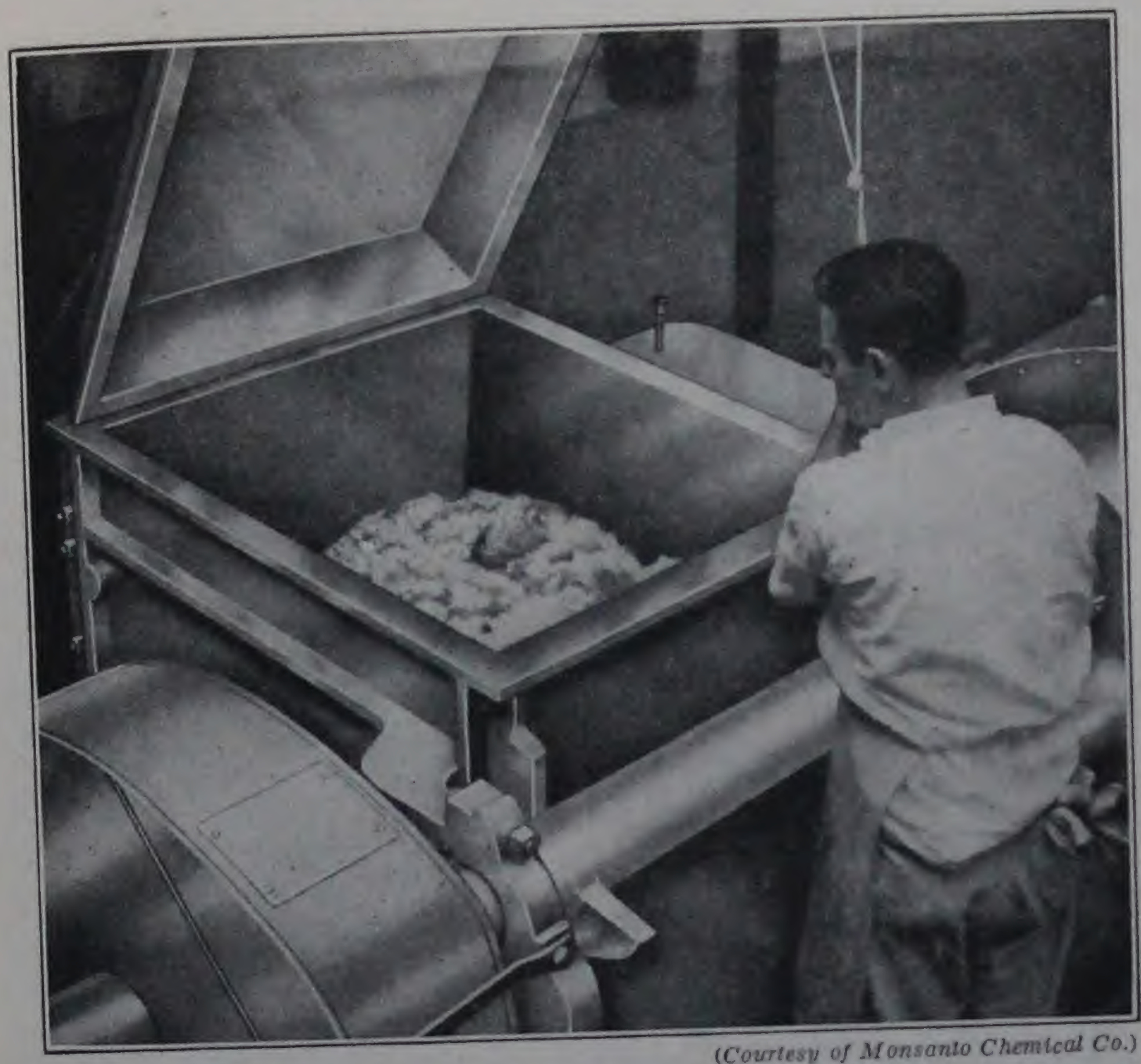
(Courtesy of Monsanto Chemical Co.)

Fig. 3-5. Centrifuge Wringer for Cellulose Nitrate.

3-6. Production of Cellulose Nitrate.—As the next step in the manufacture of cellulose nitrate, the nitrated linters are placed in a large mixing and kneading machine, together with about 10 per cent of alcohol, if the method of drying by the addition of alcohol is used. The plasticizer is next added. For this purpose, camphor is almost universally used, the proportion being approximately 30 per cent by weight.

The machine for kneading nitrocellulose, shown in Fig. 3-6, is similar to a dough mixer, in which two oppositely revolving U-shaped blades catch the material between them. The kneading operation is continued until the fibrous appearance of the nitrocellulose disappears and a homogeneous plastic mass takes its place.

At this point, coloring matter may be added. The dyestuffs are usually dissolved in alcohol or some other suitable material, and are kneaded with the mixture until the color is thoroughly uniform. According to the more recent practice, however, the color is not



(*Courtesy of Monsanto Chemical Co.*)

Fig. 3-6. Kneading Machine for Cellulose Nitrate.

added in the mixer. Instead, the kneaded material is removed from the mixer and forced through a screen by hydraulic pressure onto a rolling mill, where the color is added.

A rolling mill, shown in Fig. 3-7, consists of two large steel cylinders that revolve in opposite directions. These rolls, which are designated as the front roll and the back roll, are both hollow, or cored, to allow cold water or steam to pass through. The material is passed between the cylinders, and the rolling is continued until the color is thoroughly dispersed throughout. As the plastic mass passes between the cylinders, it forms a coat on the front roll. A large knife, the length of which is the full width of the roll, is then set in position on the operator's side of the front roll, and, as the roll revolves, cuts the plastic coat from the roll in the form of blocks or sheets. These constitute cellulose nitrate suitable for molding.

As most plastic articles made of cellulose nitrate are fabricated, it is desirable to leave the material in sheet form. In common

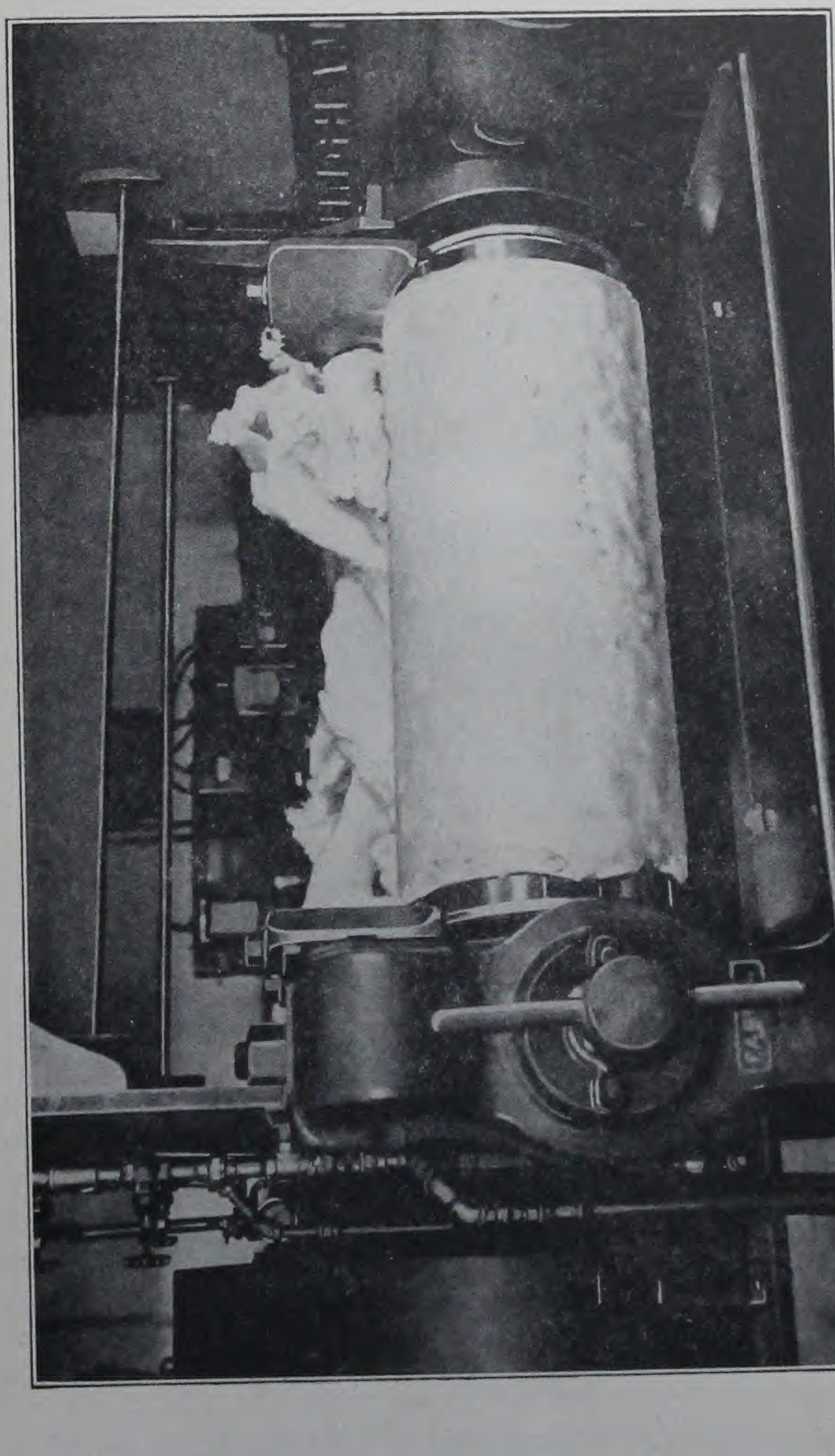
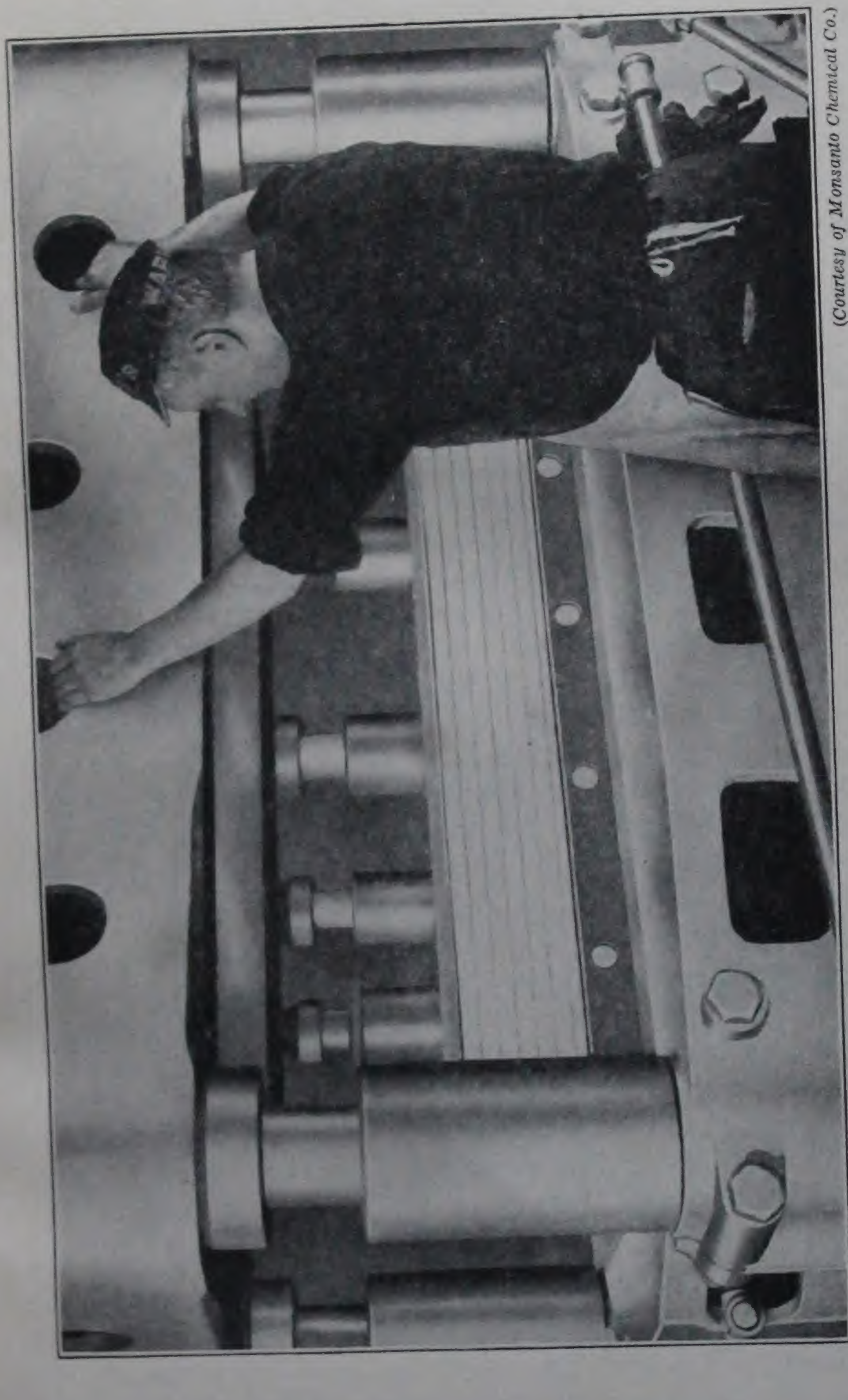


Fig. 3-7. Rolling Mill for Cellulose Nitrate. (*Courtesy of Nixon Nitration Works*)



(Courtesy of Monsanto Chemical Co.)

Fig. 3-8. Cake Press for Cellulose Nitrate Sheets.

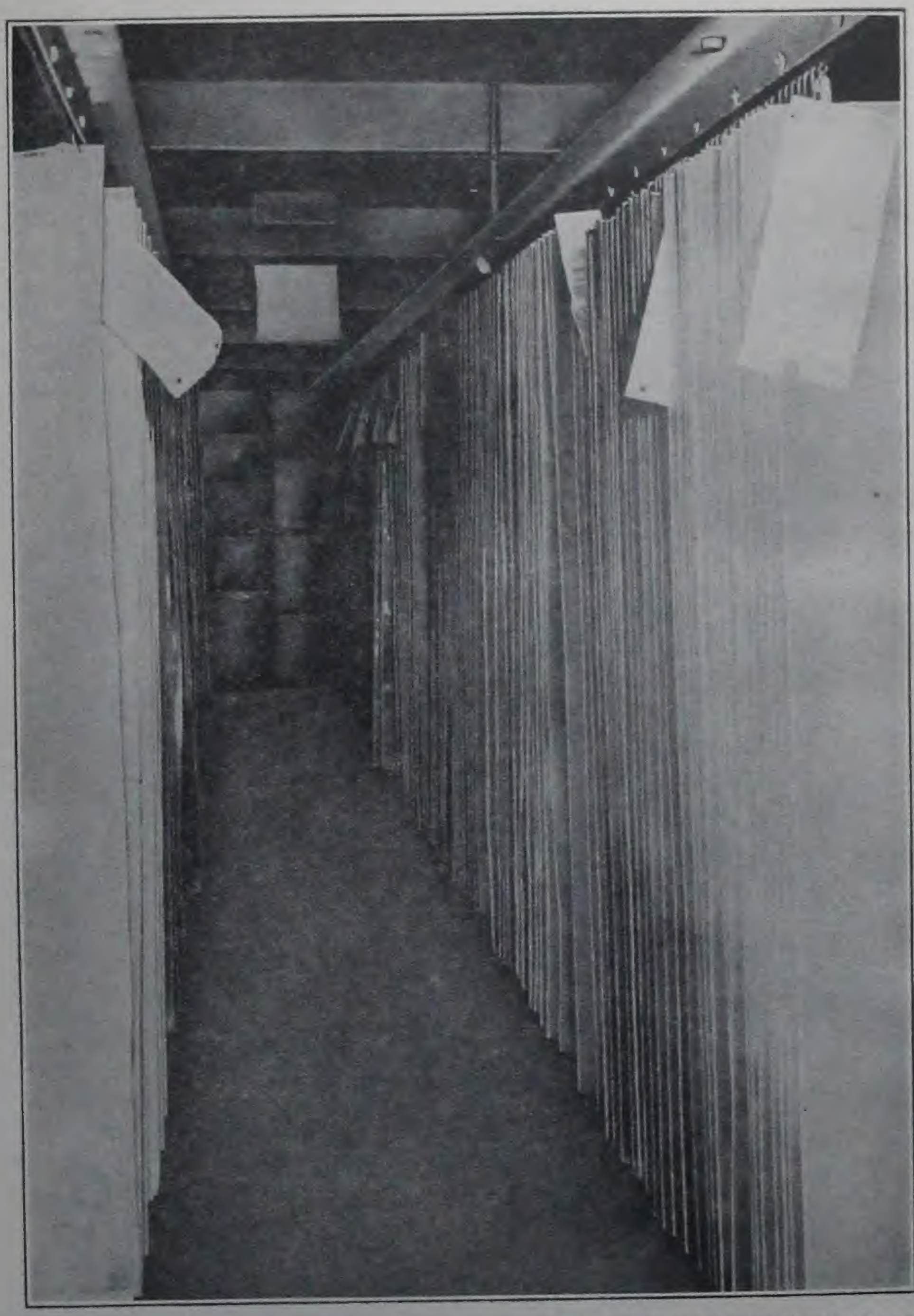
practice the sheets are stacked and then pressed into large blocks, as shown in Fig. 3-8. Since there is still some moisture in the material, it must be removed by seasoning, for, if it is not removed, it will cause warping of the articles made from the material later on.

3-7. Producing Mottled Effects.—Many of the cellulose-nitrate articles appear with grains or mottles, such as are seen in the barrels of pencils and fountain pens. These mottled effects are produced before the material is seasoned. The block of plastic is baked in an oven at about 200° F to remove air bubbles, and is then placed in a slicing machine, where sheets of any desired thickness may be cut away. Grained or mottled effects are achieved by ingenious manipulation of these sheets. For example, three solid blocks of material are available, each being approximately 3 feet by 5 feet, and they are colored red, white, and blue, respectively. The red cake is placed in a slicing machine, and sheets about $\frac{1}{4}$ inch thick are cut from it. The white and blue cakes undergo the same operation. The sheets are next stacked so that red, white, and blue layers come in regular sequence, and then are placed in a hydraulic press, where a solid cake once again is formed. This multicolored cake is placed endwise in the slicing machine, as shown in Fig. 3-9, so that the sheets cut from it have a surface appearance of grained or mottled red, white, and blue. Such a sheet, when rolled over and cemented to itself, produces a rod having red, white, and blue grains or mottles.

A tortoise-shell mottle is obtained by passing a small sheet of amber-colored cellulose nitrate through a chopping machine, which forms small amber chips. The same thing is repeated with a sheet of dark-brown cellulose nitrate. These two sets of chips are mixed mechanically in proper proportions to produce the desired effect, and are then put through a rolling mill, the rolls of which are heated to a temperature that will just soften the material. In this way a sheet of fused amber and dark-brown particles that resembles tortoise-shell is produced.

3-8. Seasoning and Polishing.—The seasoning process consists merely in removing the last trace of moisture from the material. It is usually carried on in a heated vault, such as is illustrated in Fig. 3-10. The cake of grained sheets is placed in the vault, the temperature of which is increased to a point just below the softening point of the material. The length of time for seasoning

Fig. 3-9. Slicing Machine for Materials With Mottled Effects. (Courtesy of Monsanto Chemical Co.)

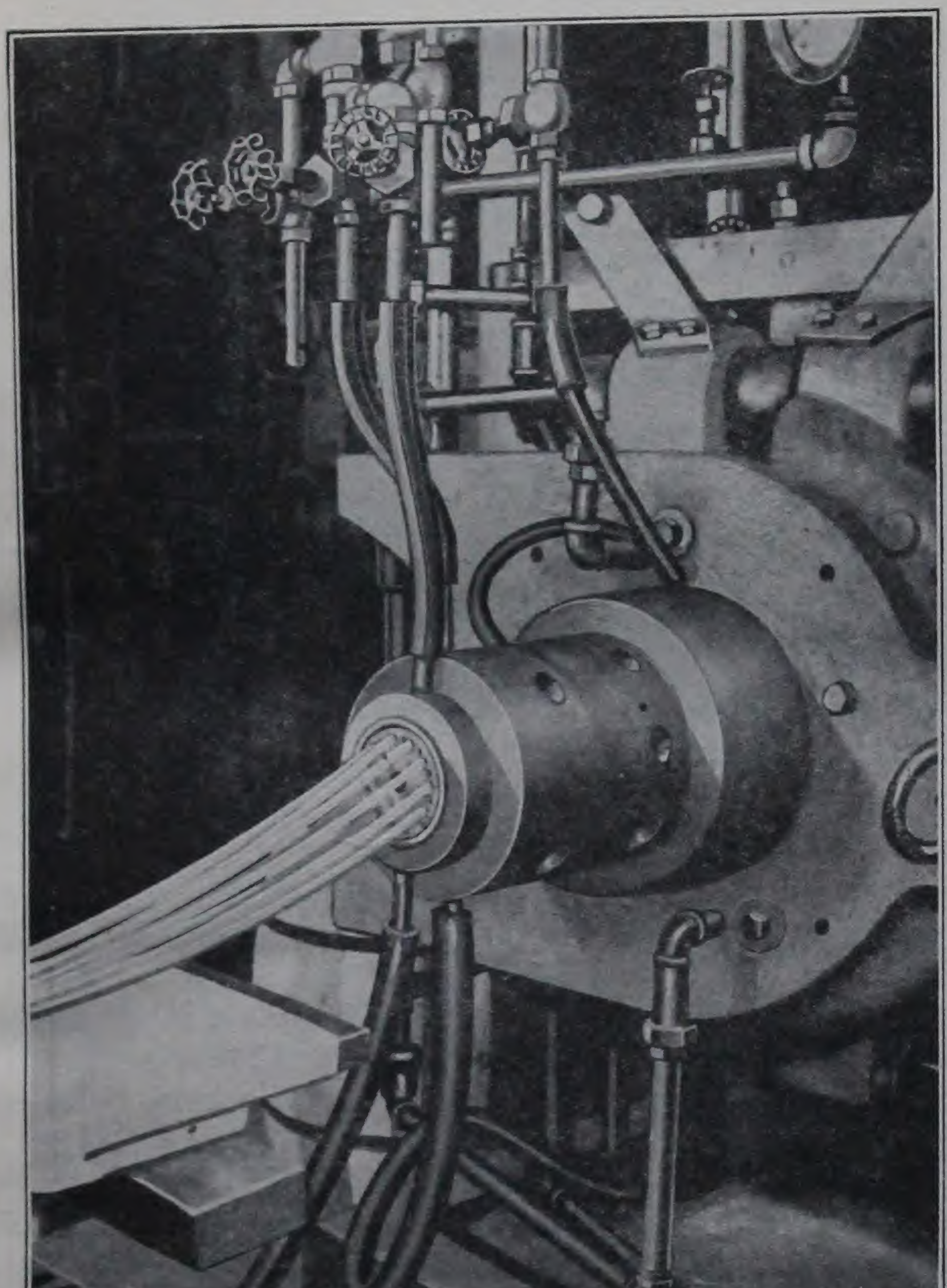


(Courtesy of Celanese Plastics Corp.)

Fig. 3-10. Heated Vault for Seasoning Sheets.

depends entirely on the thickness of the cake and the amount of moisture present. In certain cases, seasoning requires as long as several months.

After seasoning, the sheets of plastic go through a press-polishing operation, which consists in stacking them alternately

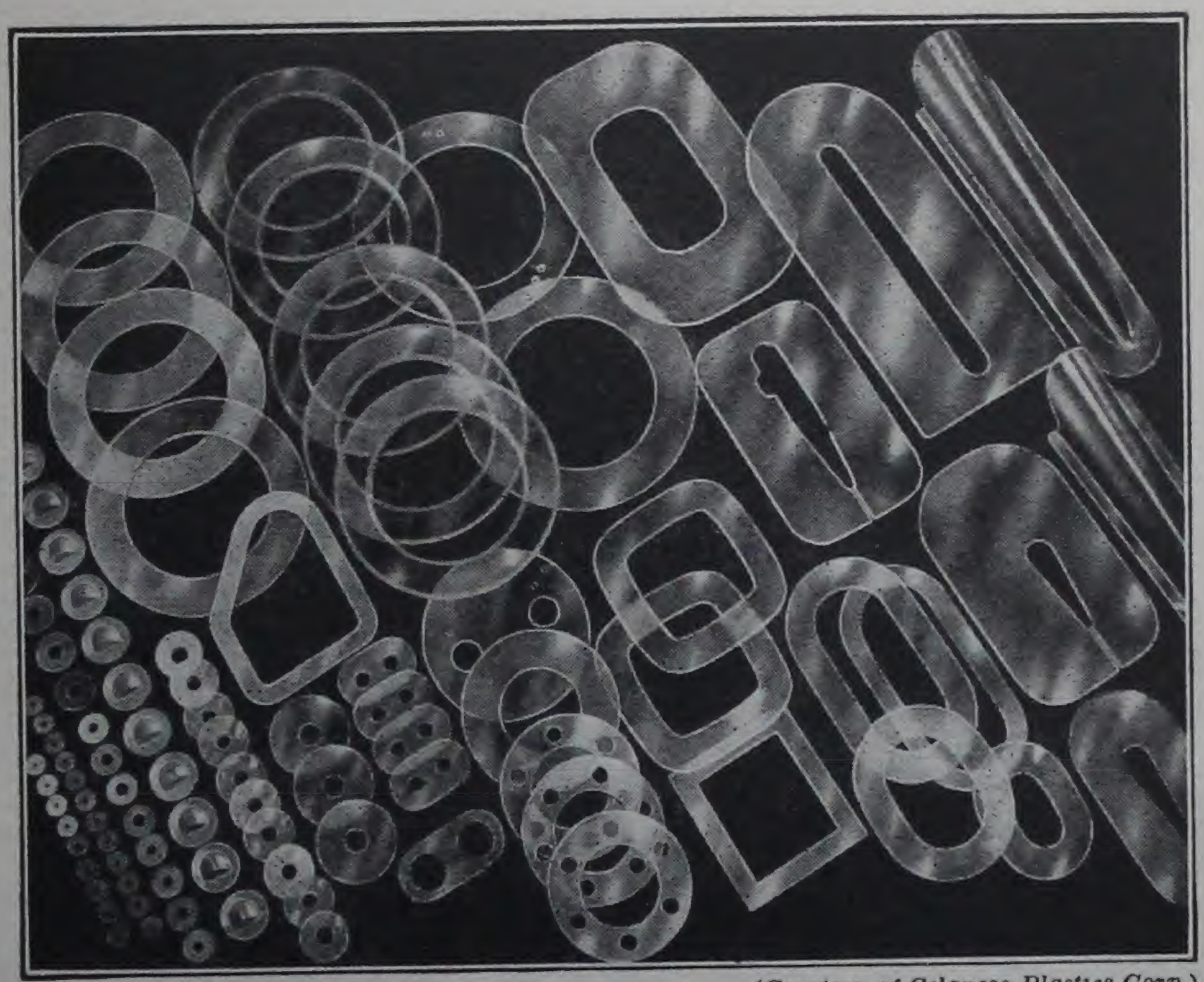


(*Courtesy of Nixon Nitration Works*)

Fig. 3-11. Extruding Machine for Forming Rods and Tubes.

with polished metal sheets, one on top of the other, and pressing them in a hydraulic press. The plastic sheets thus acquire the surface polish of the metal sheets.

3-9. Formation of Rods and Tubes.—At times it is advantageous to produce cellulose nitrate in the form of rods or tubes, rather than in sheets. To produce these forms, the homogeneous



(*Courtesy of Celanese Plastics Corp.*)

Fig. 3-12. Forms Stamped From Cellulose-Nitrate Stock.

mixture from the rolling mill is forced through dies by means of hydraulic pressure. Tubes or rods of almost any dimensions can be obtained by using the proper dies. The hydraulic equipment through which the material is forced is known as an extruding machine. Such a machine is shown in Fig. 3-11, in which the extruded material, in the form of rods, may be seen as it comes from the machine.

3-10. Summary of Manufacture.—In the manufacture of cellulose nitrate, the base, or binder, for the material is the nitrated cotton linters. The filler and the plasticizer are cellulose and camphor, respectively, the latter acting also as the lubricant. As cellulose nitrate is thermoplastic, no accelerator or inhibitor is required. A typical formula for cellulose nitrate would be as follows:

	Per Cent
Binder (cellulose nitrate)	68
Plasticizer (camphor)	30
Color (dye or pigment)	2

Cellulose nitrate is available in sheets, tubes, lacquers, rods, chips, beads, and stampings. Some of the forms are illustrated in Fig. 3-12.

Machine operations such as the following can be performed on cellulose nitrate:

Lathe turning	Swedging	Drilling	Printing
Drawing	Embossing	Punching	Blowing
Sawing	Extruding	Cutting	Molding

Cellulose nitrate can be used in the formation of a number of diversified products, such as novelties, hammer heads, pen and pencil barrels, pocketbook frames, eye-glass frames, toys, tooth-brush handles, piano keys, and drafting instruments. The material appears on the market under the trade names of Amerith, Nitron, Pyralin, Hercules Cellulose Nitrate Flake, Celluloid, and Nixonoid.

Shellac

3-11. Chemistry of Shellac.—Shellac is not an individual chemical compound. It is a solid solution of several different chemical compounds of somewhat similar structure. None of these is truly resinous when it is obtained in a relatively pure state.

The exudation of the lac bug produces two types of material—a hard resin and a soft resin. Laboratory examinations reveal that the hard lac may be broken down into four fractions. The largest division, which is approximately 40 per cent of the whole, is a composition of acids represented as $C_{32}H_{54}O_9$. The acids are composed of equal molecular proportions of aleuritic acid, $C_{15}H_{28}(OH)_3COOH$, and shellolic acid, $C_{13}H_{16}(OH)_2(COOH)_2$, both of which have been isolated, and each of which forms one of the four main fractions. The third fraction of hard lac, which amounts to approximately 20 per cent of the whole, contains aleuritic and shellolic acids and also kerrolic acid, which is represented by the formula $C_{15}H_{27}(OH)_4COOH$. The remaining 40 per cent of the hard lac consists of interesters of hydroxy acids that are similar.

The soft lac is composed of a mixture of uncondensed hydroxy acids, some wax, and a small amount of natural yellow dyestuffs.

3-12. Raw Materials.—The main ingredient of shellac plastic is shellac, the natural resin secreted by the lac bug. As a binder it leaves something to be desired; hence, other binders must be added.

For this purpose, natural gums, such as copal, kauri, and manila nubs, which are imported mainly from the Philippines and the Belgian Congo, are used.

A great variety of fillers are used, the predominant one of which is mica. Asbestos also is used in large quantities. It is a fibrous substance which, when freshly mined, is mixed with a good deal of rock. The rock must be removed. The fiber in its original form is too long to use and is broken down into what is known as "shorts." This is done by a stone mill, or Kollergang mixer. Minor fillers, such as marble dust and wood flour, are found in the natural state.

The main plasticizer is wood pitch, which is obtained by the fractional distillation of various types of soft woods. Calcium stearate and stearic wax, or stearic acid, are the most commonly used lubricants. As shellac plastics are usually manufactured in dark, opaque colors, pigments, rather than dyestuffs, are used as coloring matter. Shellac being a thermoplastic material, no accelerator or inhibitor is needed. However, in certain cases the addition of lime will greatly improve the inherent hardness of the molding compound.

3-13. Mixing of Ingredients.—A flow chart showing the production of shellac products is illustrated in Fig. 3-13. The molding compound is produced by the dry-mix method. Unlike the manufacture of cellulose nitrate, this process involves no chemical reaction, such as the nitrating of cotton linters. The shellac, which ordinarily comes as a dark-orange flake, the gums, and the wood pitch are ground to powder, as all the ingredients are used in powder form. The entire mass of ingredients is placed in a ribbon-blade mixer. This apparatus may have any one of many shapes, although the conventional mixer is shaped like a U and is several feet long. Through the center, running lengthwise, is a shaft, around which are spiral blades. At the bottom of the tank is centered a large hole that may be opened or closed by a valve. Once the materials, correctly proportioned, have been dumped into the mixer, the blades are set in motion and the mixing is continued until a homogeneous mass is obtained. The outlet valve on the tank is then opened, thus permitting the turning blades to push the material into a container placed below the tank. The premixed material is now ready for rolling.

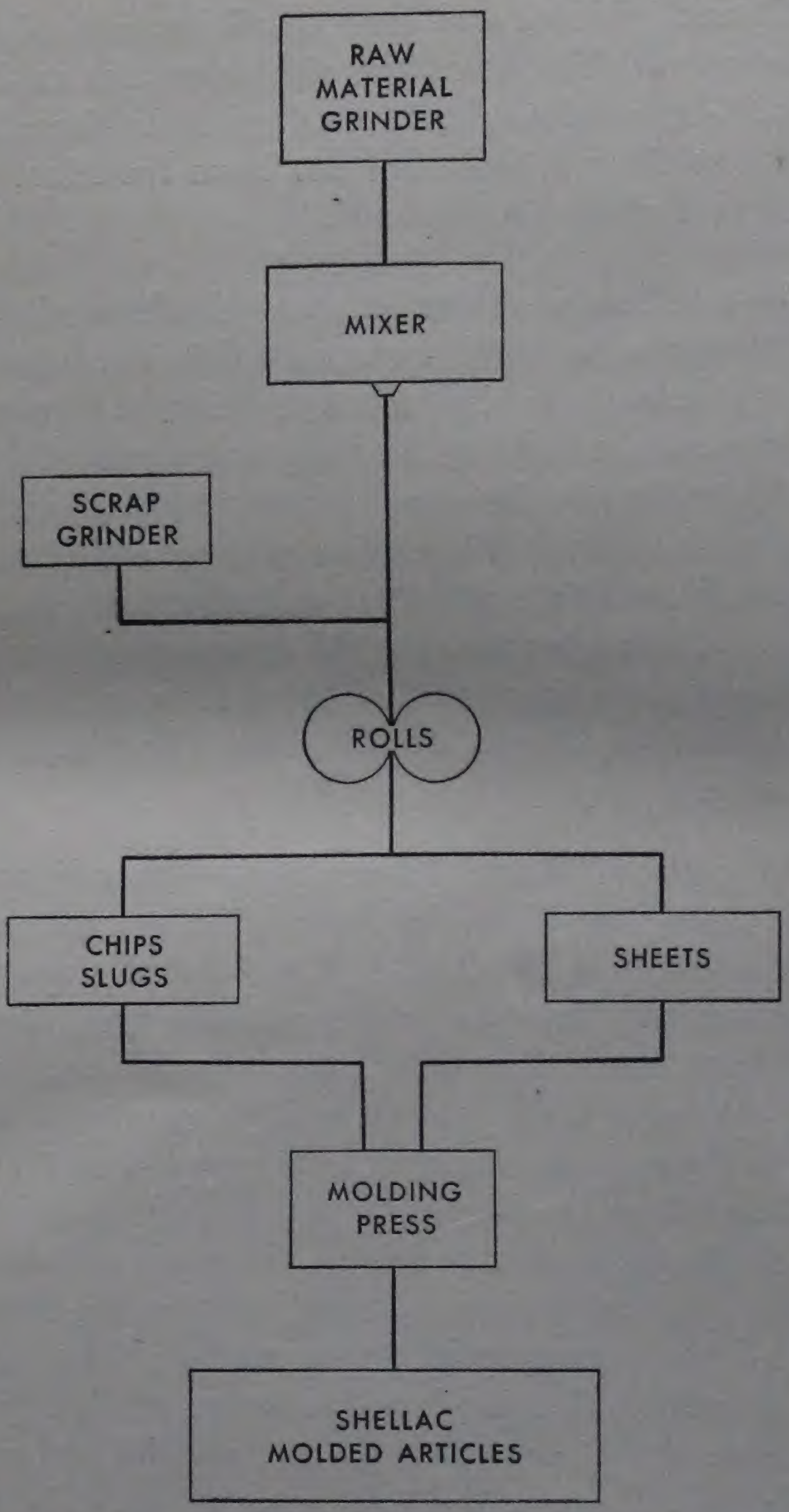


Fig. 3-13. Flow Chart for Production of Shellac Products.

3-14. Rolling.—Unlike cellulose nitrate, this shellac mixture is not combustible. Hence, the use of heat is permissible. The back and front cylinders of the rolling mill are steam-heated to temperatures of 360° F and 220° F, respectively. When the material is placed on the rolls, it absorbs heat and, owing to the temperature differential of the cylinders, it forms a coating on the front roll. As the shellac and the gums in the mixture grow warmer, they

become soft and pliable, and each small particle of the binder becomes coated with the filler. The plasticizer aids in this coating of the resin. The lubricant melts and prevents the plastic mass from sticking to the roll, but does not have the effect of making the material peel away from the roll.

3-15. Use of Scrap.—Each batch of plastic used for molding contains a certain amount of waste material. Since thermoplastic materials undergo a physical change only, all of the waste material from moldings can be used again. Such waste material is usually referred to as "scrap." The scrap is not premixed with the raw materials, but is usually run through a grinder, which reduces it to powder or granules. As the premixed material starts to soften and fuse, and scrap, which must have the same color, is added to it. The rolling process continues until all of the raw materials and the scrap have thoroughly fused. At this stage, the compound is still soft and pliable.

3-16. Removal of Material From Roll.—Directly underneath the rolls is a catch pan. When the material is first put on the rolls, not all of it adheres to the front roll and forms a coating on it. A small amount falls through the rolls into the pan. This material is recovered from time to time during the operation and replaced on the rolls. Eventually all the material will have adhered to the roll.

Below the pan is a conveyor belt having exactly the same width as the rolls and approximately 40 feet long. When the mixture is ready to be removed from the rolls, the catch pan is pushed forward so that there is nothing between the conveyor and the rolls, and the conveyor is set in motion. Also, pressure is exerted on a knife, which is pivotally mounted slightly ahead of the front roll, so that it cuts through the material and makes contact with the roll. Then, as the roll turns, the material meets the knife blade, is cut away from the roll, and drops to the moving conveyor belt. The speed of the conveyor belt is the same as that of the front roll, so that the material is carried away as fast as it comes from the roll. If the material has been properly rolled, it will be cut away in a continuous sheet. The thickness of the sheet can be controlled by regulating the space between the rolls.

3-17. Smoothing Sheet.—Owing to the heat of the front roll, the surface of the plastic sheet that was formed will be pitted and

rough. To obtain the best results in using the material, however, the surface should be smooth. Smoothness is produced by the following procedure. The temperature of the front roll is lowered by running cold water through it; then the conveyor is put in reverse and the sheet is fed over the back roll. As soon as all the material has been returned to the rolls, the knife is applied, the conveyor is set in forward motion, and the sheet is cut off. Because of the lower temperature of the front roll, the sheet becomes smooth. The material is still soft and pliable and usually must remain on the conveyor belt for about 5 minutes to cool and become rigid. As the actual rolling time of a batch is about 30 minutes, the cooling time on the belt does not interfere with further production. Another batch can be rolled while the preceding one is cooling.

3-18. Shellac Molding Compound.—Shellac material is used as a molding compound in the form of slugs or preformed shapes. These are usually made while the material is cooling on the conveyor belt, a mechanical scoring blade or hand knife being used for this purpose. When the material is cooled, the sheet is broken into the preformed shapes. These constitute shellac molding compound.

3-19. General Discussion.—The binder in shellac molding compound is a combination of approximately equal weights of shellac and natural gums. The filler, depending on the physical property to be achieved, is mica or asbestos or some other suitable material. Wood pitch is employed as a plasticizer, and calcium stearate or stearic wax is used as a lubricant. Although it is not generally needed, lime is sometimes used as an accelerator. Various pigments make up the coloring matter.

A typical formula for the manufacture of a shellac molding compound is as follows:

	Per Cent		*Per Cent*
Binder	40	Lubricant	2–3
Filler	54	Accelerator	0–1
Pigment	3	Plasticizer	2

The amount of scrap used in a batch is about six times that of the raw material. If, for example, there were 30 pounds of raw material in the mix, 180 pounds of scrap would be added. In making a new material, there is the possibility that no scrap of that

particular color is available. Common practice has been to use scrap of a closely corresponding color and to add it to the raw material on the roll. Additional coloring matter is added to the mixture while it is on the roll. This is called shading. In order to make sure that the final color will be correct, a small sample is taken from the roll and molded as a check for color. In the event no scrap is available, it is advisable to make a scrap batch. A scrap batch is a regular run of material which, when cooled, is ground and used as the scrap for the next regular batch. It has been found through experience that a material containing no scrap does not possess enough denseness to produce satisfactory molded articles.

Shellac is classed as a thermoplastic material, despite the fact that from continued use it tends to harden owing to a semi-polymerization. Scrap can be used as a molding compound by merely rerolling it without the addition of any raw materials. However, the life of the shellac is thus lost.

The time at which a mix on the rolls is finished is best determined by the eye. Since shellac is composed of many hydroxy acids, there is a possibility of water being formed if the shellac begins to undergo any chemical change. Mixing it too long on the rolls will cause bubbling, with resulting puffs of gas coming from the material. When this occurs, one can be certain that the limit of the shellac rolling operation has been reached. If the coloring matter has not been thoroughly dispersed throughout the material, it is necessary to add more shellac on the roll. This acts as a revitalizer until thorough dispersion has taken place.

3-20. Applications of Shellac.—Shellac, in the form of slabs, sheets, and variously shaped slugs, may be processed by compression, extrusion, or injection molding. A few of the applications of shellac are electrical insulators, weather-board, buttons, phonograph records, outdoor telephone equipment, dominoes, checkers, etc. Shellac has been used as a protective coating for floors and for cables. These are not direct uses in the plastics industry, but it is well to note them. Other such uses are as sizing in paper, as binders for hat felt, and as dressing in the machine-belting and leather industries.

3-21. Trade Names.—It is peculiar that no commercial source of supply of shellac molding compound exists. The manu-

facturer usually compounds shellac to his own specifications. For that reason, the trade names Complac, Harvite, Lacanite, and Composite are given the materials of commerce.

Cold-Molded Compounds

3-22. Chemistry of Cold-Molded Compounds.—When natural resins, such as copal, asphalt, or dammar, are used, there is no chemistry involved, since all these substances are thermoplastic and merely undergo physical change. The first cold-molded materials were made with binders of this nature. Later, however, newer developments introduced synthetic resins of the phenolic type as binders. Materials of this kind present a definite chemical picture. Since the volume of cold-molded materials, compared with other plastics, is small, the discussion of the chemistry of the synthetic phenolic resins used as binders will be fully treated under the discussion of phenolic plastics.

Cold-molded compounds may be borderline compounds of the natural-resin or synthetic-resin type. In general, they are divided into two classes, namely, organic, or non-refractory; and inorganic, or refractory. These classes are not to be taken as generic classes for plastics as a whole, but apply only to cold-molded plastics.

A refractory material may be defined as one that is difficult to melt or burn. Cold-molded compounds that use either synthetic resins or natural resins as binders fall into the first-mentioned class. The inorganic type has portland cement as its binder. Although compounds of the inorganic type have been used as plastic materials in products like porcelain insulators, they are better known in the roofing industry. Wet mixtures of asbestos and cement, suction-filtered and then pressed into forms, have been used for many years to produce the so-called asbestos-cement roofing shingle. Since this is somewhat removed from what is generally thought of as plastic molding, it is mentioned merely to complete the materials list.

3-23. Raw Materials.—The binders for the organic type of cold-molded compounds consist of synthetic resins of the phenolic type. Of these there are innumerable varieties, all of which are produced by the chemical condensation of phenol and formaldehyde. Many bituminous binders are used, such as gilsonite, which is a glossy form of asphalt. Fillers such as asbestos, clays, mica,

and wood flour are all natural substances. As with shellac plastics, stearic wax and waxes of a similar nature are used as lubricants. In general, cold-molded compounds are produced in only black and dark-brown colors. Carbon black and earth pigments, such as umber and sienna, are acceptable as coloring agents. As with other thermoplastic materials, the plasticizer plays an important part in flow characteristics and in imparting improved chemical and physical properties. Some of the many plasticizers used are tricresyl phosphate and chlorinated biphenyl. Both are synthetic products of chemical manufacturers. In cold-molded compounds, no accelerator is used. In its place, vulcanizing or oxidizing agents, such as sulfur or lead oxide, are used. The function of these agents is to convert the plastic mass during the mixing stage from tacky globules to non-tacky granules.

3-24. Method of Manufacture.—A flow chart showing the steps in the production of cold-molded articles is given in Fig. 3-14. The first step in the manufacture of cold-molded compounds is the preparation of the binder. A blend of various natural and synthetic resins, such as copal, gilsonite, and dammar, in conjunction with stearic wax, is placed in a kettle and digested, or cooked; and to it the plasticizer is added. The mixture, which soon thickens, as does that used in the manufacture of varnish, is cooked until it is thoroughly homogeneous. While it is cooling, its viscosity is reduced by adding a mixture of thinners and solvents that are compatible. A free-running liquid will wet, or impregnate, dry fillers much more readily and thoroughly than does a highly viscous liquid.

While the binder is being prepared, the filler is loaded into a kneading machine of the Baker-Perkins U-blade type. This machine differs from the U-type spiral mixer in that it has only two blades. These, rotating in opposite directions, knead the material. The machine is set in operation and then the binder, which has been thinned and heated to about 240° F, is poured in. The filler and binder begin to mix immediately; and, when distinct separation between the binder and filler in no longer noticeable, the coloring matter and the oxidizing agent are added. The mixture is then kneaded until homogeneity is obtained. Continued kneading beyond this point causes the mixture to change from a tacky mass into a material with a granular structure. When converted

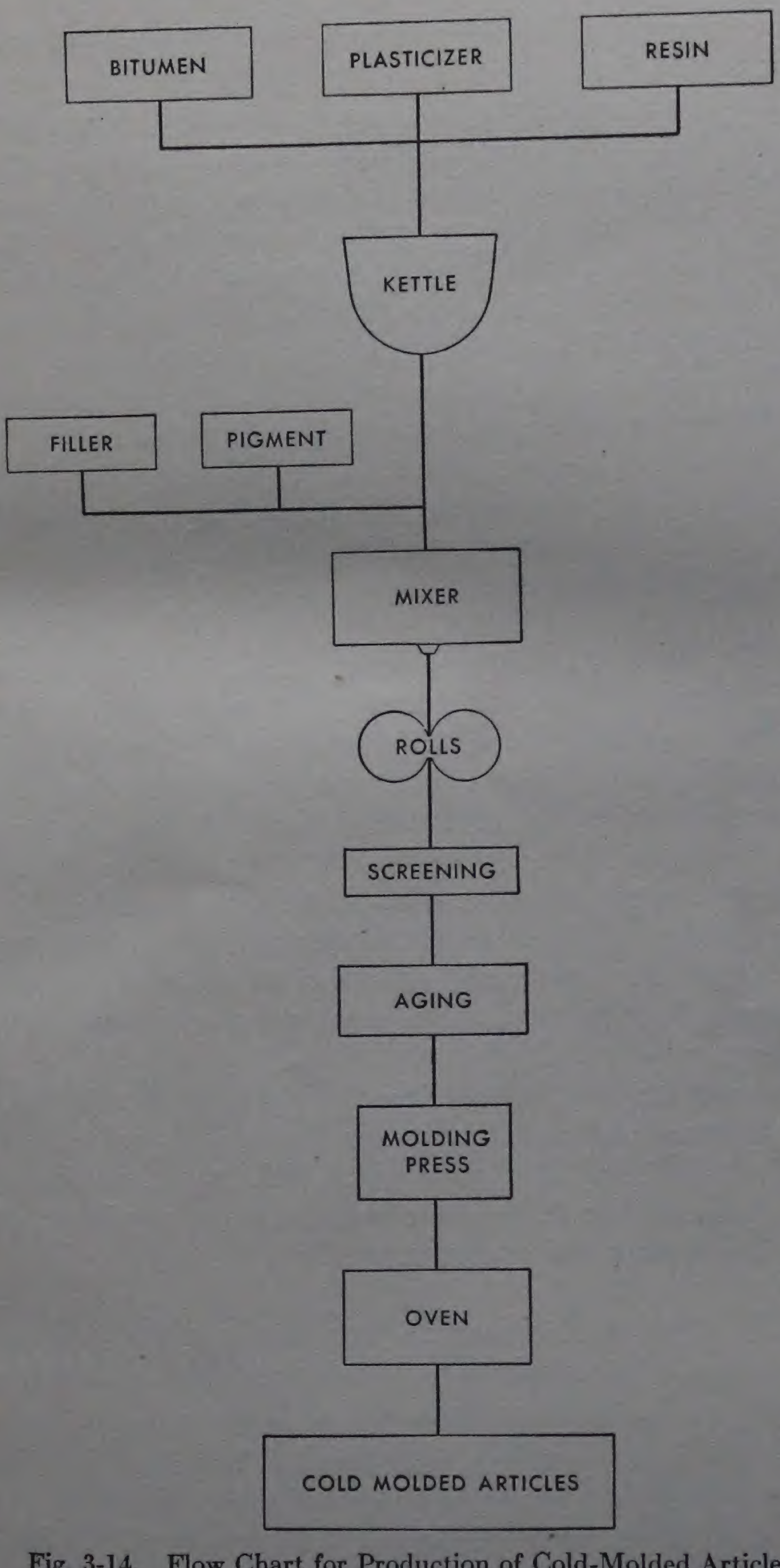


Fig. 3-14. Flow Chart for Production of Cold-Molded Articles.

to the granular stage, the material is ready for discharge from the mixer.

The next operation is a screening or sorting of the granules, or particles, according to granular size. This is important, as in the subsequent molding operation the sizes of the particles must be uniform. Some manufacturers prefer to pass the granules through a rolling mill to form a sheet. The sheet is then put through a pulverizer, which definitely controls the granulation. Regardless of which method is used, the granules must be seasoned.

The seasoning operation consists in merely allowing the granules to be exposed to the air so that any excess solvent will be evaporated and the compound will be stabilized by absorbing moisture from the atmosphere. The aging period is usually about 24 hours. The resultant material is cold-molded plastic suitable for the molding operation.

3-25. Molding and After-Baking.—Thermosetting compounds are molded under heat and pressure, but cold-molded plastics, as the name might imply, are molded only under pressure. The heat is supplied by an after-bake treatment, during which enough heat must be supplied to thermoset the synthetic binder. The temperature is increased from 150° F to 400° F at the rate of approximately 10 degrees per hour. The temperature increment is purposely kept low in order to maintain the dimensions of the article. It is during this slow curing operation that the oxidizing agent comes into play. Slow oxidation helps prevent warpage and excess shrinkage.

In cases where no synthetic resin is used in the binding mixture, the after-bake treatment causes the hardening of the thermoplastic natural resins and gums, along with the vulcanizing agent. The hardening is a chemical change and the resultant plastic object is a thermosetting plastic.

3-26. General Discussion.—The binder in a cold-molded compound may be entirely natural resin or entirely synthetic resin, or a combination, in any proportions, of both.

The filler, depending on the physical property to be achieved, is any inert substance such as asbestos shorts or mica.

The plasticizer, depending on the flow and to a certain extent on the chemical properties to be obtained, may be one of the

phosphate family, such as tricresyl or dibutyl phosphate, or a chlorinated biphenyl. Each manufacturer has special plasticizers for various purposes.

The lubricant used to prevent sticking in the molding operation is a metallic stearate, such as aluminum stearate, or a neutral soap, such as stearic wax.

The coloring matter, depending on whether black or brown is desired, will be carbon black or sienna.

The usual vulcanizing and oxidizing agents are, respectively, sulfur and lead oxide or selenium.

In the production of a cold-molded compound, a typical formula would be as follows:

	Per Cent		*Per Cent*
Binder	25–28	Oxidizing agent	8
Filler	60	Lubricant	0.25
Pigment	2	Plasticizer	2

3-27. Applications and Trade Names.—The available forms of cold-molded compounds are granules and preforms, which are converted into such articles as handles and knobs for cooking utensils, connector plugs on toasters and irons, valve wheels, and liquor closures.

As in the case of shellac materials, there is no commercial source of supply from which cold-molded plastic materials may be purchased. Each manufacturer that has use for this type of material makes his own. The formulation of the compound will depend on the type of application of the finished object. Some trade names given by the individual manufacturers are Aico, Textolite, Coltstone, Gummon, and Thermoplax.

Chapter Four

Phenolic Plastics

Types of Phenol-Formaldehyde Products

4-1. Groups of Phenol-Formaldehyde Plastics.—Phenol-formaldehyde plastics are classified as thermosetting materials of the synthetic resin type. Figuratively they have many thousands of different kinds of applications. It is only natural, then, to find that they are divided and subdivided into many groups. The first, and probably the largest, of the groups contains the molding compounds. The second large group consists of the cast phenolics. Some objects that are molded are not made of a true molding compound, but are formed from somewhat similar materials known as Rogers Board and Rogers Blanks. These objects constitute the third large group of phenolic plastics. The fourth large group contains the laminated phenolics. Two other groups worth mentioning are the phenolic-pulp compounds and the phenolic-asbestos compounds.

4-2. Phenolic Molding Compounds.—Molding compounds of phenol formaldehyde are of six general types, each of which is intended for a specific kind of application. These types are the following:

General purpose	Low loss
Heat resistant	Transparent
Impact	Special duty

In most instances, the filler is responsible for the differences between the types. The solid materials used in any molding compound are ground to a powder or into small particles before they are incorporated in the mixture.

The general-purpose compounds are used for applications that do not require special properties. Molding compounds of this type probably are most commonly used where decorative articles are to be produced. The filler in such compounds is usually wood flour, but ground nut shells are also used.

The heat-resistant type of molding compound uses asbestos as a filler. The difference between a compound to be used for high heat and one for medium-high heat depends on the per cent of asbestos in the formula. This type finds use as handles and knobs for cooking utensils and stoves.

The impact materials are used where resistance to a sharp blow is required. Several types of fillers can be employed, the best one depending on the degree of impact strength required. For a medium impact, ordinary cotton linters or flock can be used; for a higher impact, small pieces of canvas are used; and, where the highest degree of impact is encountered, pieces of rag or sisal fiber are employed.

The low-loss materials find their greatest application in electrical and radio insulation. The filler in these cases is ground mica or spun glass. These materials give the best results where high dielectric strength and low power factor are of prime importance.

It has been stated that fillers are mainly responsible for certain properties of a compound. However, the transparent type contains no filler. It is this absence of filler that gives the material its transparency. In a transparent compound the resin acts as both binder and filler.

Each special-duty compound is made to fit a specific use. For instance, a compound may be required to withstand a certain oil at a temperature of 425° F, and to maintain a relatively good impact strength. No general-purpose material, heat-resistant material, or impact material alone will meet this specification. It is necessary to formulate a special-duty compound that will serve the purpose. This is accomplished by incorporating several fillers in one formula.

4-3. Cast Phenolics.—Phenolic plastics of the cast group, like the transparent types of molding compounds, contain no fillers. The binder is manufactured in such a manner that the plastic can be poured into molds, cast, and given an after-bake treatment, as is done with the bituminous type of plastic. The after-bake treatment is a process of heat treating a material or object to produce rigidity. Cast materials invariably need finishing operations. The article coming from the lead mold requires polishing. About 50 per cent of the plastic jewelry of the better kind is made from cast phenolic materials.

(Courtesy of Union Carbide and Carbon Corp.)

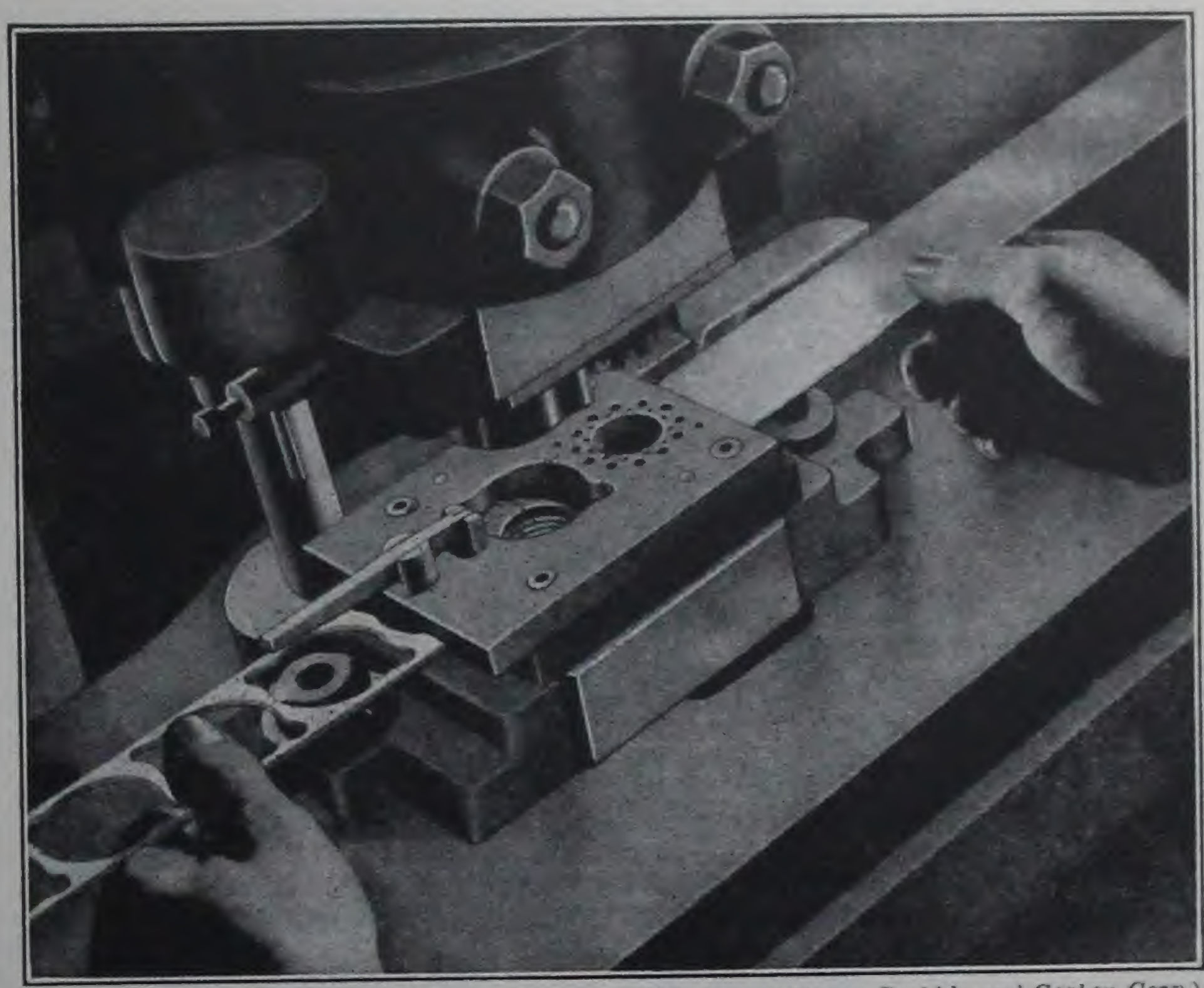
Fig. 4-1. Pouring Liquid Resinoid Into Radio-Cabinet Lead Molds.

In Fig. 4-1 liquid resin is being poured into lead molds for radio cabinets. An after-bake operation is required for a complete hardening of the compound. Pressure from a pneumatic hammer will remove the cast cabinet. The removal of the rough edges, with subsequent polishing, results in a cast-resin radio cabinet.

4-4. Rogers Board and Rogers Blanks.—Materials known as Rogers Board and Rogers Blanks are similar to molding compounds in that filler and resin are used. The forms, however, are different. The resin is used to impregnate paper or cardboard filler. When dry, the blanks are punched out according to the sizes and shapes required for the articles. These punched blanks are used like articles made of a molding compound. A blanking operation is shown in Fig. 4-2.

4-5. Laminated Phenolics.—The group of phenolic plastics known as laminates is divided into the following three types:

General purpose
Impact
Special duty



(*Courtesy of Union Carbide and Carbon Corp.*)

Fig. 4-2. Punching Machine for Phenolic Board Stock.

The principle of lamination involves the impregnation of a filler, such as ordinary newsprint, kraft paper, linen, or canvas. Instead of preparing the filler as individual sheets, it usually appears in roll form. Large sheets of the impregnated filler are cut from the roll and stacked on top of one another. The subsequent molding operation fuses all the sheets into a solid mass. Restaurant-table tops are examples of such lamination. The choice of filler will depend on the application of the laminate. An impact laminate which is to be used for gears in a machine will have roll-canvas as the filler. The choice of filler with laminates is the same as the choice of filler with molding compounds.

4-6. Phenolic-Pulp Compounds.—Phenolic-pulp material is used for special purposes to bridge the gap between molded phenolics and laminated phenolics. Molding compounds, owing to the fillers used, have been produced with various properties; but in molding operations the filler and resin may separate, thus producing sections of uneven strength. The laminated group, for all practical purposes, is limited to flat or very simple articles. The pulp-resin combination to a certain extent overcomes the shortcomings

of both molded and laminated compounds. It is a comparatively recent development, and not much information is available with respect to its commercial possibilities.

4-7. Phenolic-Asbestos Compositions.—A number of phenolic-asbestos compositions have been developed for structural use. These compounds differ from the heat-resistant molding compounds in that large sections for acid-resisting and alkali-resisting tanks can be made from them. Sections as large as 10 feet×12 feet have already been formed. The asbestos in this type undergoes special treatment to make it acid-resistant.

Materials for Phenolic Plastics

4-8. Baekeland-Bender Theory of Resin Formation.—The chemistry of the phenolic plastics is complex. Many thousands of different types of resins have been made and are in use in conjunction with phenolic compounds. Basically, they all are made by the same chemical reaction. Since all phenolics come under the heading of synthetic resins, it is necessary to make the synthetic resin before a molding compound can be formulated. There are two major theories on the formation of this resin, which are known as the Baekeland-Bender theory and the Blumfeldt theory.

In applying the Baekeland-Bender theory, phenol is mixed with formaldehyde and hydrochloric acid, the latter being used as a catalyst. The reaction takes place in a nickel-lined, jacketed kettle. Heat is applied to the mixture, which is constantly agitated. After a short while, the chemical reaction starts. Since it is exothermic, the reaction continues after the source of heat is removed. It is often necessary to run cold water through the jacket of the kettle to control the reaction. Upon completion of the reaction, it will be found that a resin has formed.

A large volume of water is produced during the reaction, and an examination will show two distinct layers in the kettle, namely, the resin layer on the bottom and the water layer on the top. The water is removed by allowing the layers to separate and then carefully pouring the top layer off; this pouring process is known as decantation. The last remaining traces of water are removed by distillation. The viscous amber-resin that remains in the kettle is the synthetic resin used in the manufacture of molding compounds. The resin is poured from the kettle onto a steel floor or into metal

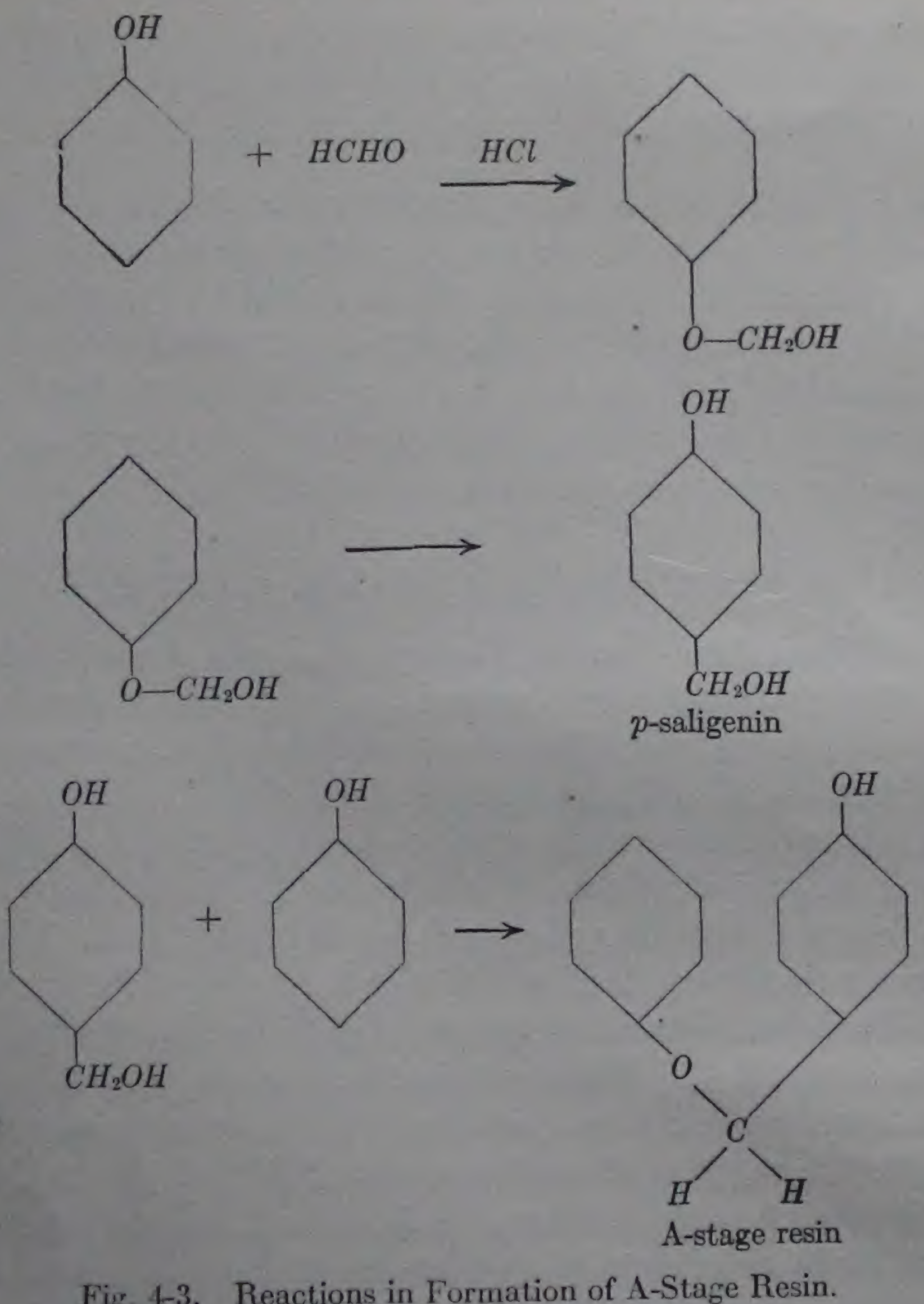
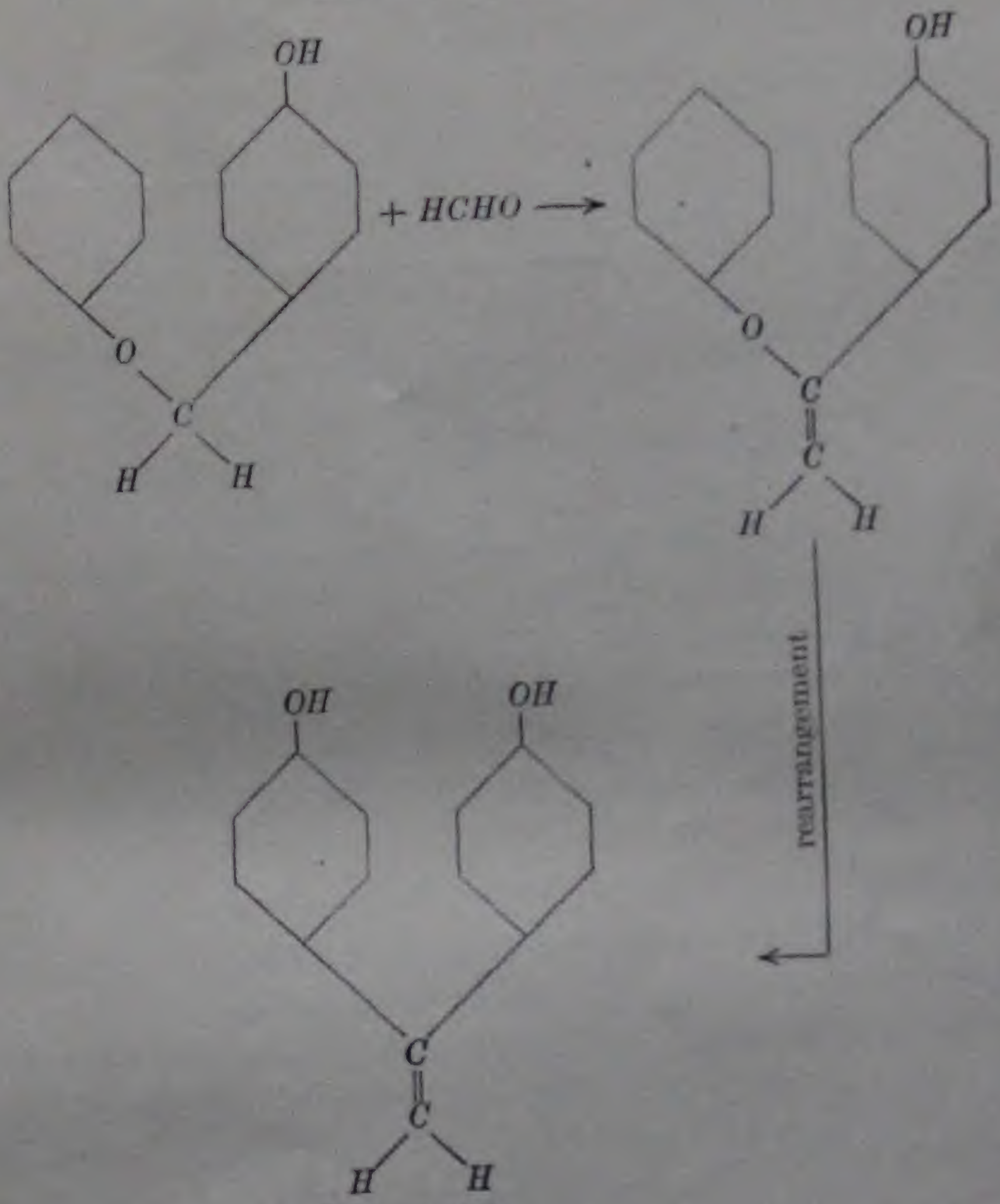


Fig. 4-3. Reactions in Formation of A-Stage Resin.

trays. On cooling, the resin becomes hard and brittle, and it is then ground into a fine powder and stored for subsequent operation.

According to the concepts of the Baekeland-Bender theory, one mol each of phenol and formaldehyde combine to form *o*-hydroxy benzol alcohol, or *p*-saligenin. This product then condenses with a mol of phenol to produce the unsymmetrical ether, *p*-hydroxy-phenylphenoxymethane, which is fusible and soluble and is called the A-stage resin. Condensation of the foregoing unsymmetrical ether with a mol of formaldehyde, followed by a minor rearrangement, forms what is called the B-stage resin. The chemistry of the formation of the A-stage and B-stage resins is shown by the reactions in Figs. 4-3 and 4-4.



B-stage resin

Fig. 4-4. Reactions in Formation of B-Stage Resin.

4-9. **Blumfeldt Theory.**—The Blumfeldt theory of resin formation is based on reactions involving the use of an alkaline catalyst. The equipment and process are the same as those described in the preceding article, but the chemistry is somewhat different. Phenol and formaldehyde are placed in the kettle with ammonia as the catalyst. The chemical reaction starts to take place on the addition of heat, and it subsequently supplies its own heat through an exothermic reaction. The decantation and distillation procedures are the same as those outlined in the discussion of the Baekeland-Bender theory.

The chemistry of resin formation according to the Blumfeldt theory is outlined by the reactions in Figs. 4-5 and 4-6.

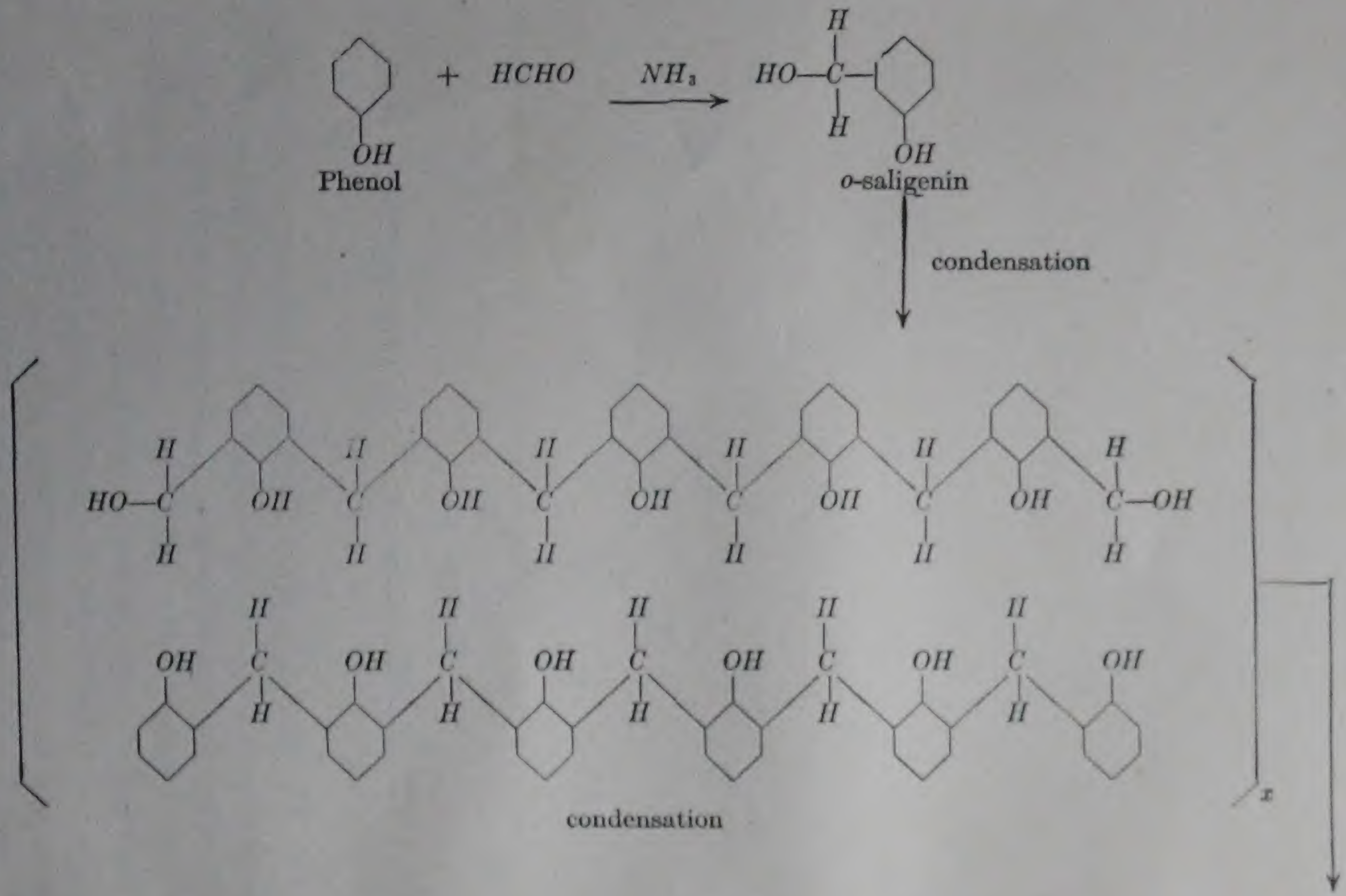


Fig. 4-5. First Reactions in Blumfeldt Theory of Resin Formation.

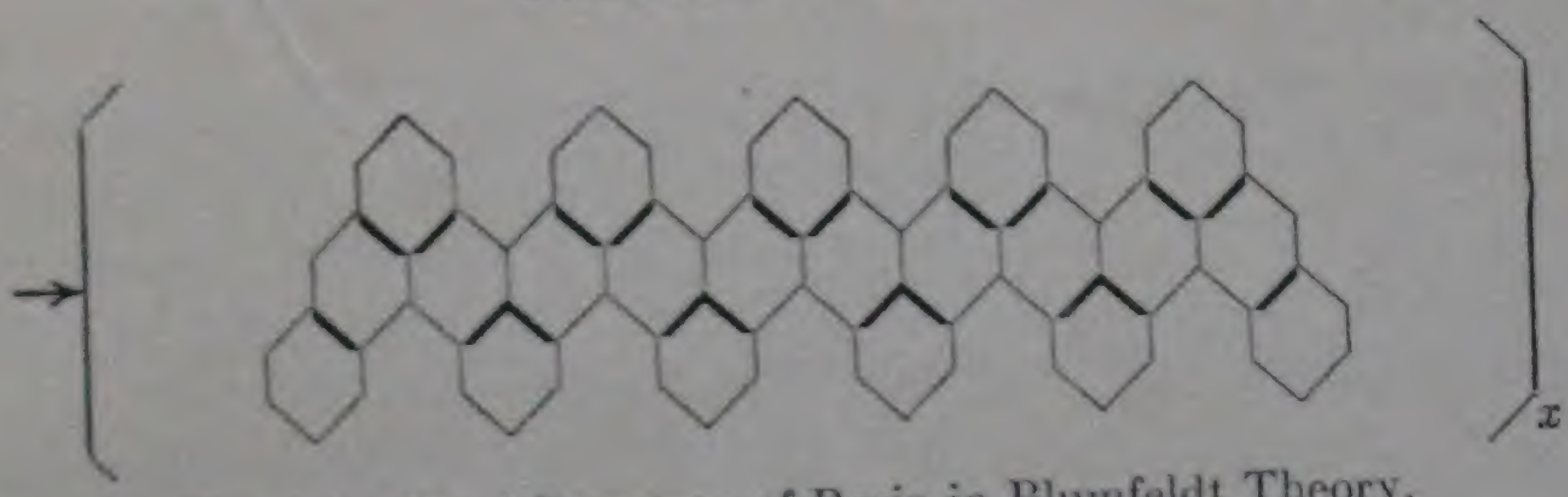


Fig. 4-6. Final Structure of Resin in Blumfeldt Theory.

4-10. Comparison of Theories.—It will be noted that in the Baekeland-Bender theory the *OH* group and the CH_2 group are at opposite ends of the benzene ring. These are known as the para positions. The Blumfeldt theory shows the two groups adjacent to each other, or in the ortho positions. In the Baekeland-Bender theory, the *p*-saligenin reacts with another molecule of phenol to produce the A-stage resin. From the Blumfeldt point of view, a number of molecules of *o*-saligenin condense to form a complex resin.

The difference between the two theories is supposedly due to the nature of the catalyst. Both theories are acceptable. When the resin is tested for anisole, $CH_3OC_6H_5$, oxygen is found. It is known that anisole is present in some form in the resin. On this basis, the Blumfeldt theory appears to be in error, since no oxygen appears in the final formula. This can be explained logically by assuming that one CH_2OH group remains in the resin. The one oxygen atom will reveal itself in the anisole test.

4-11. Phenol.—Of the many raw materials used in the production of synthetic phenolic resins, phenol is by far the most important. However, cresol or derivatives of cresylic acid are suitable. Phenol was formerly obtained as a by-product in the distillation of coal, but the amounts produced in this manner were insufficient to meet the demand for the material. Most phenol today is produced synthetically from benzene and air in the presence of a catalytic agent by means of the Raschig process, which is one of the more important developments of our times. Cresols and their derivatives have not yet been produced synthetically; they are obtained in the distillation of coal and wood.

4-12. Aldehydes.—Many aldehydes are used in the production of phenolic resins. Probably the most important of these is formaldehyde, which, in its natural state, is a gas. In the plastics

industry it is usually found in a 37% water-solution called formalin. Formaldehyde has two main sources. The first is the oxidation of methyl alcohol, and the second is the synthetic process of reacting carbon monoxide and hydrogen. The latter method is the larger producer.

4-13. Types of Fillers.—The fillers used for phenolic plastics fall into two major classes—inorganic and organic. The type of phenolic compound will, in most cases, dictate the kind of filler to be used. The group of inorganic fillers, such as asbestos, have high heat-resistance and good insulation properties. The organic fillers, such as wood flour, have the advantage of low specific gravity and good surface appearance in the molded article. Common fillers for all the various types of molding compounds are wood flour, mica, cotton flock, asbestos, and diatomaceous earth. In general, a filler should possess the following characteristics:

Easy wettability
Low moisture absorption
Low abrasive quality
High impact strength
High tensile strength
Low surface tension
Inertness to acid and alkali
Inertness to solvents
Freedom from odor

4-14. Wood Flour.—In general, wood flours contain soluble resinous matter. The smaller the amount of this material present, the better the filler. Pine, spruce, and poplar make good fillers. The color of the wood is also important, since it is bound to impart its own color to the molding compound. All the woods mentioned are light in color. For certain special-duty materials, the harder and darker woods, such as maple and oak, have been used successfully. Uniformity in the wood structure is another essential characteristic. The wood must be free from knots and bark, as they affect the hardness, color, and chemical composition of the wood.

The wettability of the filler is very important. By wettability is meant the extent to which the filler is coated by or absorbed into the resin. The soft woods are the easiest to wet; the hard woods are almost unwettable. If wetting does not take place, specks and spots of the filler will show up in the finished molded article.

Wood flour is used in a ground state. Grinding is just as important as the choice of the wood. A fibrous filler will give the best strength in a molding compound. However, if the fibers are

too long or too thick, many manufacturing difficulties arise. The fibers in wood are alined in the direction of the grain. Correct grinding of wood breaks the fibers lengthwise rather than cross wise. In this way, the strength of the fiber is not reduced. Grinding of this nature is called *attrition grinding*. Particles that pass through a 100-mesh sieve are acceptable as filler.

4-15. Fillers for Impact Materials.—Recent developments have brought about a large increase in the use of impact filler materials. These materials have been made available through the use of new type fillers which basically possess impact strength greater than that of wood flour. The filler to be used will depend on the degree of impact strength required. Cotton flock is probably used more than any other material for impact strength. It is necessary to control the length and density of the fiber. This control is somewhat easier to attain than with wood flour, since the fibers of impact fillers are individual. Materials with higher impact strength are also made with a cotton base, which is used as patches of woven cloth, rather than the individual fibers.

Strips of canvas make one of the best fillers for the higher types of impact materials. In addition to the strength of the fiber, the strength of the weave is also obtained. Sisal rope and tire cord have also been used to some extent as fillers for shockproof plastics. Care must be taken that the color of the fiber used does not interfere with the color of the finished plastic material. In addition the fiber should have a low moisture absorption.

4-16. Fillers for Heat-Resistant Materials.—The heat-resistant plastics, with few exceptions, use asbestos as a filler. The term *asbestos* usually refers to any fibrous material that is mined. In the plastics industry, asbestos usually refers to hydrated magnesium silicate, the common name of which is chrysotile. As mined, asbestos fibers are rather long and grouped. Best results are obtained from this type of filler when it is defiberized and broken down into small particles. Because high-heat materials, as a rule, are chosen for an application for their heat-resistant nature and not for strength, it is not important that the fibrous character of the filler be retained to obtain maximum strength. If the material is left in a fibrous form, streaking and sticking will always occur in the molding process.

4-17. Fillers for Low-Loss Materials.—Diatomaceous silica is the outstanding non-fibrous mineral material used as a filler. This type of filler finds its greatest use in the low-loss electrical field. Its outstanding characteristics are low loss on ignition and low moisture content. The disadvantages are its abrasiveness and high bulk factor. Mica is another material that is used in the low-loss class. Its chief disadvantage is its inability to be wet by the binder. It is also very abrasive in its action on steel molds.

4-18. Other Fillers.—Several other fillers have been developed for the general-purpose type of molding compound. In addition to having good characteristics as a filler, they possess certain inherent plastic qualities. They contain definite resinous elements that actually serve in conjunction with phenolic resin as binders in the molding compound. Examples are the ground shells from walnuts, peanuts, and pecans. Walnut shells contain approximately 30 per cent of lignin and about 4 per cent of cutin, the latter being a wax. When activated, both of these resinous bodies have the properties required of a binder. Unfortunately, the percentages are not high enough to use the shells alone, and it is necessary to augment them with phenolic resin. The shells obtained from the nut growers always contain a certain percentage of nut-meat, which must be removed by extraction or incineration. The dry nut shell is then ground to a size suitable for use as a filler.

4-19. Dyestuffs and Pigments.—Phenol has the unfortunate characteristic of changing color on exposure to light. The resin formed from phenol and formaldehyde has a light amber color. In some extreme cases, in order to produce a water-white material, a blue or violet dyestuff is added to help counteract the natural yellow color produced by the phenol. Since the phenolics are generally produced in dark colors, this yellowness does not have any bad effects.

The coloring of phenolic plastics presents many problems. Dyestuffs are affected by the acidity of a compound. A blue dyestuff in a highly acid compound may exhibit a green color. A dyestuff maintains its color only within certain temperature ranges; so, if the heat used in making or molding a compound is too great, the dyestuff will lose its color. Characteristics of a good coloring agent are: stability to heat, stability to light, solubility, and chemical effect.

Wherever possible a pigment should be used as the coloring agent. Most pigments have all of the foregoing characteristics except solubility. The solubility problem can be overcome by later milling operations. A pigment cannot be employed in a transparent plastic, as light would not be transmitted through it. In such instances, acid dyes and mordant dyes have been found to give the best results. Since the phenolics are mainly produced in black and brown, the main coloring agents are carbon black and burnt or raw umber.

Cost is an element in the manufacture of any material. The dyestuffs are always much more expensive than the pigments. It is true that dyestuffs, when dissolved in solvents, have greater covering power, but this advantage is usually offset by their increased cost. Since there is no white dyestuff, the only method of producing a white color is to use titanium dioxide or some white compound of zinc, calcium, or barium. Recent developments have proved that titanium dioxide exists in two forms, namely, *rutile* and *anatase*. The covering power of anatase is greater but, since rutile is cheaper, it will probably replace anatase. The difference between the two is in chemical structure.

Many novel effects can be produced by the use of special dyestuffs. Fluorescence and phosphorescence are obtainable in phenolic plastics by the addition of dyes; but the phenolic resin has a harmful effect on dyestuffs of this nature, and it is necessary to use large quantities of dye to obtain any appreciable result. Most of the novel effects are obtained by using cellulose and other thermoplastic materials, with which a small percentage of dyestuff will bring about the desired result. The usual amount of dyestuff is about 2 per cent of the total weight of material.

4-20. Lubricants.—In molding materials of the phenolic type, lubricants are definitely needed. Although it is not a rule, it may generally be said that the more fibrous the filler, the more a lubricant is needed. Usually two lubricants are used in the manufacture of a phenolic plastic. Dual lubrication arose from the two distinct processes the material goes through. One lubricant must be incorporated to prevent sticking in the molding operation. Another lubricant must be incorporated to prevent sticking in the manufacture of the material itself. If both lubricants in their original amounts are present in the molding compound, the molded

articles usually have a dull surface appearance. Therefore, the lubricant that is used to prevent roll sticking should be of such nature that it will volatilize during the manufacture of the plastic and will be lost. The other lubricant remains in the compound to serve its purpose in the later molding operation.

The choice of lubricants is easily accomplished by employing materials with wide differences in melting points. Lubrication is usually thought of as a reduction of friction between surfaces. Where friction is high, heat is generated which causes sticking between the surfaces. Various waxes, such as montan and carnauba, are successful in reducing friction in the material manufacture. Calcium stearate or zinc stearate serves the same purpose in the molding operation. Since chromium is a slippery metal, many surfaces where friction occurs in machines used in the plastic industry are chrome-plated. This practice is not absolutely necessary in the case of plastomic plastics, but it helps a great deal as a lubricating factor.

4-21. Accelerators and Retarders.—Thermosetting synthetic resins are somewhat difficult to control. The difficulties can usually be attributed to the incorrect chemical stage of the resin, or binder, which affects the molding operations. The reaction in which the resin was formed may have proceeded beyond the point considered as best for molding procedures. On the other hand, the reaction may not have reached its ideal stage of development. Accelerators and retarders are used to bring about a correction in the resin.

A resin that is chemically underdeveloped is termed a *slow resin* and needs an accelerator to speed up the later reactions that the resin must go through. On the other hand, when the reaction in the kettle has gone too far, the resin is termed a *fast resin* and, in order to control it in subsequent operations, a retarder must be used. This has the effect of slowing down the further chemical reaction of the resin. The most widely used accelerator is ordinary lime, which seems to be able to chemically excite the internal structure of the phenolic resin. Waxes such as paraffin are used as retarders. The wax may be thought of as an excess of lubricant. Most of the paraffin is lost in the process of material manufacture. However, its presence during the processing is sufficient to delay the reaction.

It has been proved by experiment that either an accelerator or a retarder has a direct bearing on the electrical properties of the material. In cases where the material is to be manufactured for electrical use, great care must be taken to use the minimum quantity of accelerator or retarder. The best practice is to make sure that the resin needs no speeding up or slowing down.

4-22. Plasticizers.—In molding compounds of the thermo-setting type, it is always necessary to make certain that the material remains in the plastic state long enough to flow and completely fill out the article to be molded. The term "fill out" may be defined as the flow of material in a die to form a completely molded article. An article that is imperfect because of lack of material is said to be "not filled out." In most cases, the hardness or softness of the compound will take care of fill out. In certain exceptions, such as long-draw articles, it is necessary to add a plasticizer. Common oils, such as tung oil and soy-bean oil, are used for this plasticizing action. Since materials of this type affect the chemical and physical properties of the molding material, their use should be avoided as far as possible.

Production of Phenol-Formaldehyde Plastics

4-23. Three-Stage Development of Phenolic Plastics.—The production of the final molded article of a phenolic plastic involves three so-called stages of development. Baekeland first named the three stages the A-stage, the B-stage, and the C-stage, when he observed that the transformation of phenol and formaldehyde to an insoluble, infusible resin took place in three steps, or stages. These terms are still used, although the division between two successive stages is not entirely clear cut.

In the A-stage the resin is in the form of a thick liquid which is hardenable by heat to a final infusible and insoluble condition. It is an intermediate product that has reacted to the stage where it is soluble in acetone and becomes thinner on heating. In the B-stage the resin has reacted to the point where it softens but does not melt on heating. It swells in acetone, but does not dissolve. In the final stage, or C-stage, the resin is insoluble in acetone, is infusible, and shows no softening on heating. The finished molded article is therefore in the C-stage of development.

In the B-stage the material is always an insoluble solid that can be softened by heating for a limited number of times before it

is converted into the infusible, insoluble C-stage final product. In the A-stage, the material is generally a liquid, although it may be a pasty solid. The transformation from the B-stage to the C-stage is generally considered as a polymerization process. The transformation from the A-stage to the B-stage probably involves both condensation and polymerization processes, although the polymerization is not complete until the C-stage is reached.

An A-stage resin, under ideal conditions, is soluble and fusible. By allowing a condensation reaction to proceed too far, polymerization of the resin starts. This means that the resin to be used as a binder in the formation of the molding compound has advanced too far and will need a retarder. If the condensation does not proceed far enough, the resin will be slow and will need acceleration in the processing stage. The polymerization reaction in the B-stage definitely depends on the condition of the resin in the A-stage. The complete polymerization in the final molding of the compound will depend entirely on the extent of polymerization in the B-stage.

4-24. Use of Accelerator or Retarder to Attain Correct Three-Stage Development.—Graphic representations of correct and incorrect stages of resin development are illustrated in Fig. 4-7. In diagram (*a*), a line 1 inch in length represents the proper A-stage and a line of the same length represents the correct B-stage. The diagram shows that the resin has been made properly to produce the correct B-stage. The rolling operation is accomplished in the correct time, and no change in the formulation, such as the addition of an accelerator or a retarder, is necessary.

In the case represented in diagram (*b*), the condensation is incomplete and the resin is not a full A-stage resin. If the position of the division between the A-stage and the B-stage is compared with the normal position indicated by the dotted line, it will be noted that the A-stage is only about one-half complete. The B-stage is necessarily incorrect because the A-stage is not complete. This diagram adequately illustrates the condition of a "slow resin." In order to rectify the condition, it is necessary to add an accelerator to the formula. When the rolling operation takes place, the accelerator stimulates the resin so that the net result of the A-stage and the B-stage is the same as the norm.

Contrasted to the condition of a slow resin is the condition of a "fast resin," illustrated in diagram (*c*). The A-stage, compared

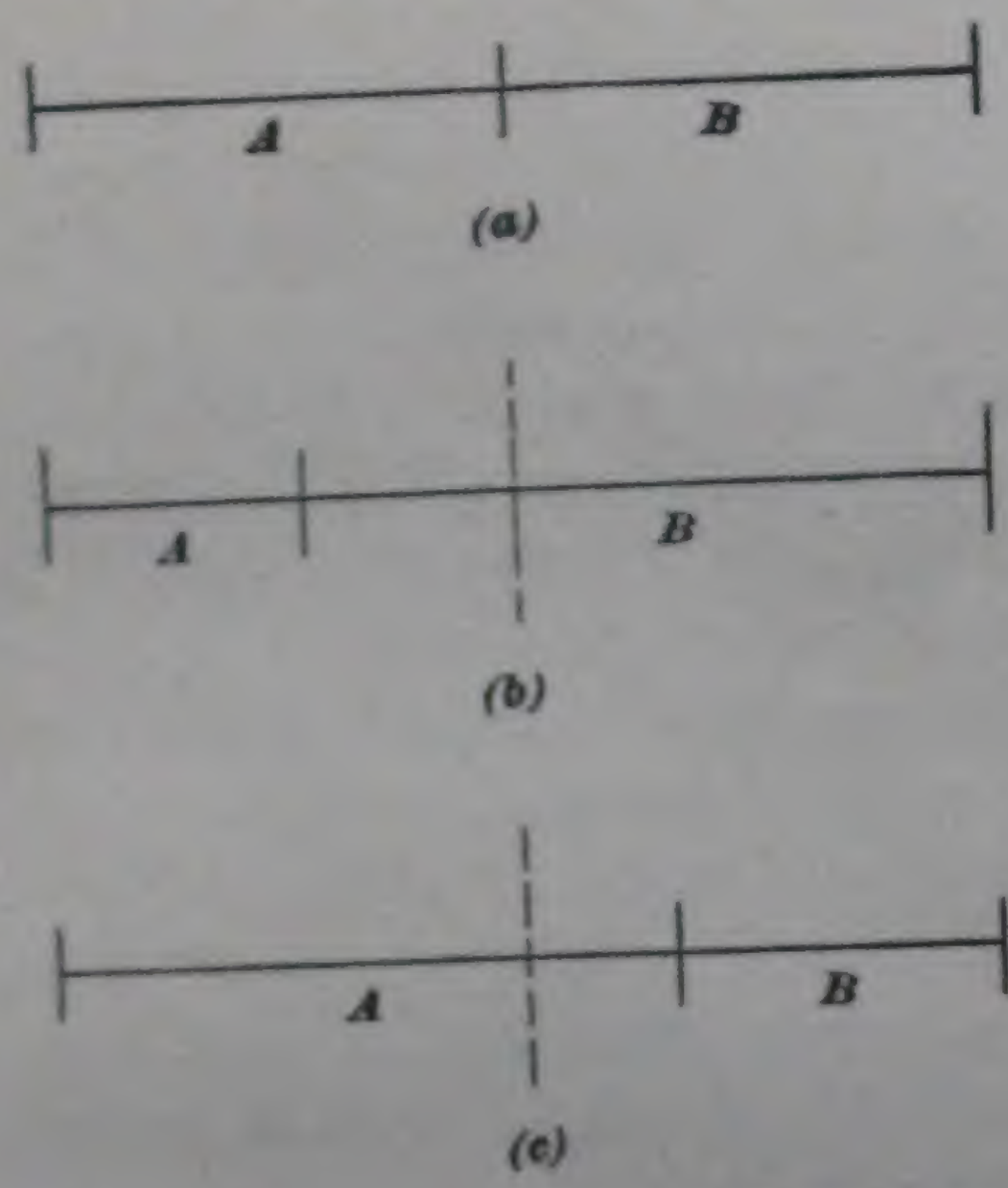


Fig. 4-7. Graphic Representations of Correct and Incorrect Stages of Resin Development.

to the norm, extends beyond its limit of correct development. This resin has already started to polymerize. It has infringed on part of the B-stage. In order to compensate for this condition, a retarder is added to the formula. The retarder slows down the activity of the resin in the rolling operation so that the net result of the A-stage and the B-stage is comparable with the norm.

A resin can be tested and checked to determine if it is a full A-stage resin, or is slow or fast.

4-25. **Adjustment of Rolling Conditions.**—There is another way to compensate for a slow or fast resin. Instead of changing the formula, the rolling conditions are changed. The material may be accelerated or retarded by raising or lowering the temperature of the rolls, but this method is not so satisfactory as changing the formula. An attempt to change roll temperatures to compensate for a deficiency or excess in A-stage development usually leads to mechanical trouble in the rolling operation. While the temperature change might adjust the A-stage correctly, the material will have a tendency to peel away from the roll if the temperature is too low or to burn fast to the roll if the temperature is too high.

4-26. **Flow Requirements.**—A molding compound of the general-purpose variety may be used for many different applications. Some articles may be small and easy to mold, such as a

button. Others may be large and more difficult to mold, such as a box for playing cards. While the chemical composition is the same, there must be differences in the plasticity of the material. The degree of plasticity is usually referred to as *flow*. Experience has shown that different types of articles require material of different flows. In the manufacturing stage, it is necessary to consider not only the type of phenolic but the flow as well. In molding compounds, where a general-purpose material is required, it is incorrect practice to use a heat-resistant material merely because the flow of the heat-resistant material is better suited to the job.

Flow is measured in many different ways. The simplest method would be to force a weighed amount of material through an orifice under known conditions of heat and pressure for a definite length of time. The distance that the material will move through the orifice under these conditions can be measured in inches or a fraction of an inch. For example, if the material moves through a distance of 2 inches, it may be said that the material has a flow of 2. If another material is subjected to the flow test under identical conditions, and this material flows through a distance of only $1\frac{1}{2}$ inches, it is said that the flow of the second material is $1\frac{1}{2}$.

4-27. **Methods of Changing Flow of Given Type of Compound.** Each individual type of phenolic material can be made with a variety of flows in either of two ways. The first, and probably the easier, is to vary the per cent of binder in the formula. As long as the type of filler remains the same, the kind of compound will be the same. An additional amount of resin yields a softer compound, while less resin produces a harder compound. There are limits as to how much or how little binder can be used. If an insufficient weight of binder is used, the filler cannot be properly covered and spots will appear in the article. If too much binder is used, sticking and high cost of compound will result.

When the flow would have to be such that the high limit or the low limit of binder content would be exceeded, the second method should be used. This involves changes in the duration of the rolling operation. The B-stage is a semipolymerizing stage. As the material absorbs heat from the rolls, the molecules become larger and, consequently, the material becomes less plastic. By lengthening the rolling time, the flow can be reduced because the

material becomes harder; and, by shortening the rolling time, the flow can be left greater.

4-28. Correction of Flow of Rolled Material.—In some instances, the rolled material may become too hard or too soft, as a result of an error in judgment or some mishap in the rolling process. Material that is too hard can be placed in the blender and softened by the addition of a small amount of lubricant. Great care must be taken in an operation of this character, as too much lubricant will cause dullness in the molded article. If the original formula contains the maximum amount of lubricant, this method cannot be used unless the article is of such a nature that a dull surface will not make any difference.

Material that is too soft can be stiffened by adding an accelerator to it in the blender. The material can never be put through a second rolling operation, however, since the crushing pressure and temperature on the rolls would permanently harden the material almost immediately. Material that is too soft may be hardened in an oven or a heated room at about 100° F. This small amount of heat will have the effect of slowly polymerizing the resin and thus making the compound harder. The length of time required for such an operation will depend on how much harder the material must be made. Hardening of a material may also be accomplished by a simple blending of the soft material with a harder material.

4-29. Obtaining Mottled Effects.—Grained or mottled effects may be produced in phenolic materials. If the mottle is to be a splash of red and black, two batches—one of red and one of black, and both having the same flow—are made. The two batches are then dumped into the same blender, and the mechanical mixing produces the mottled material. If the mottle is to be predominantly red, then a greater proportion of red material will be used.

If the mottle is to be streaked to simulate the grain of a wood, two batches of the required colors are made. The color that will eventually be the streaks is made in a softer flow. Both materials are placed in the blender, and they are mechanically mixed. Subsequent molding of this mixture will cause the softer part of it to flow in and about particles of the harder material.

4-30. Flow Chart for Phenolic Molding Compounds.—In Fig. 4-8 is shown a flow chart for phenolic molding compounds. It shows the steps from the raw materials to the finished compound.

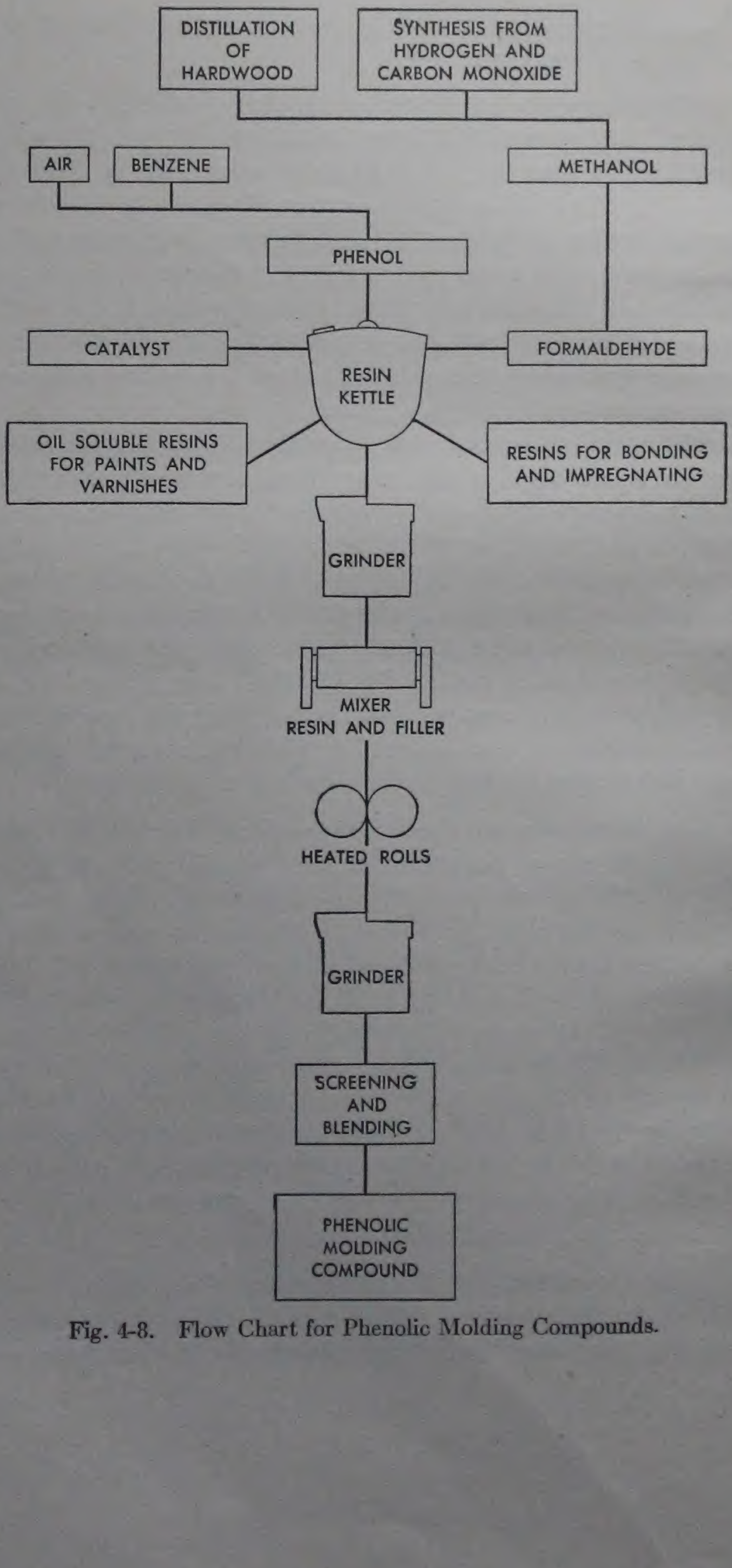


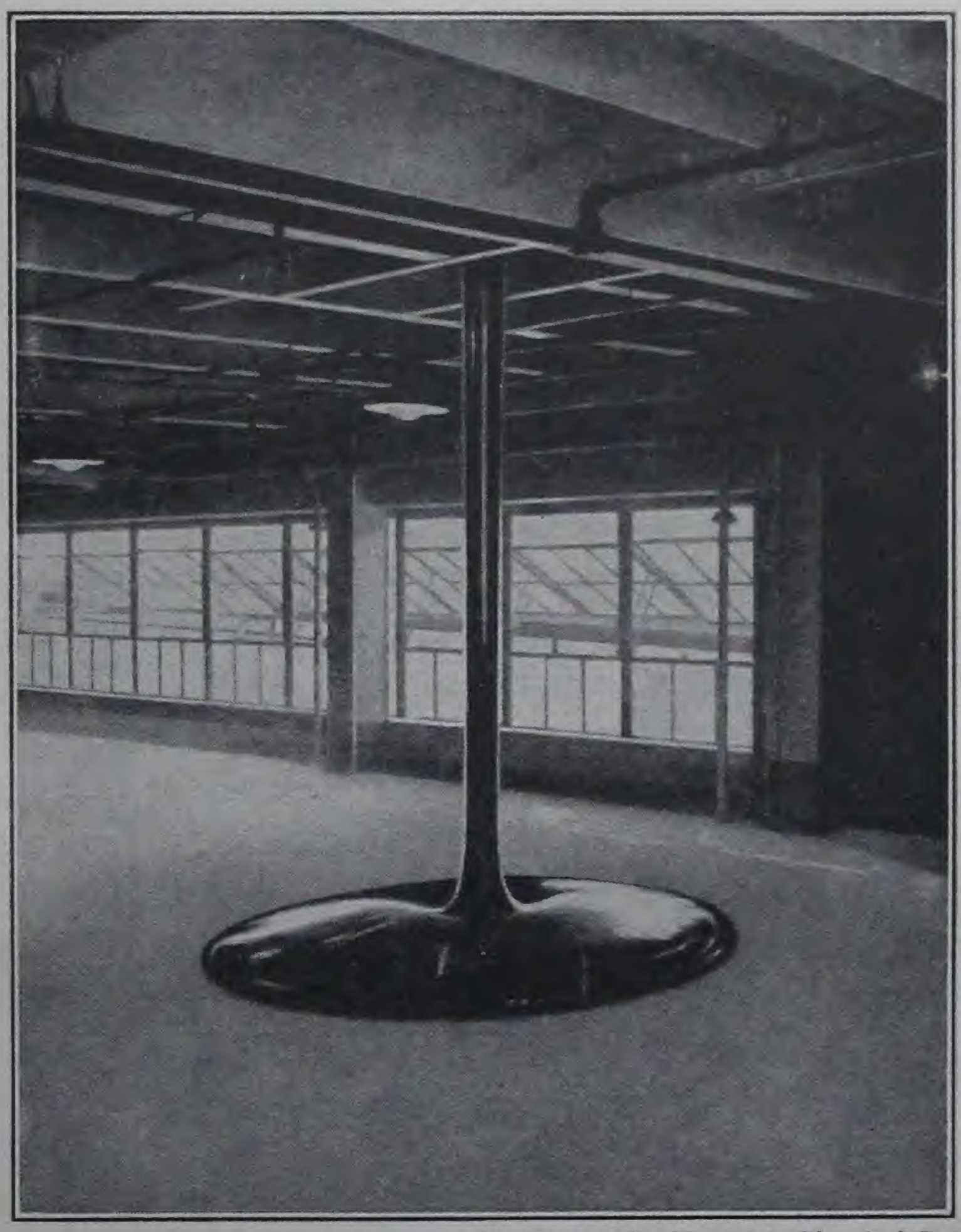
Fig. 4-8. Flow Chart for Phenolic Molding Compounds.

4-31. Manufacture of Phenolic Resin.—In the manufacture of phenolic resin, a definite charge of phenol is mixed with a definite amount of formalin. The resin can be made in either of two ways, but the same results are obtained. In order to produce light-colored resins for the manufacture of colored molding compounds, the one-stage process is used. In the one-stage process, the complete charge of phenol and formaldehyde is placed in the kettle. The reaction is started by means of heat, the source of which is removed when the action gets under way. When condensation is complete, the remaining resin is known as a one-stage resin.

In the two-stage process for making resins, the first operation is to place the full charge of phenol in the mixing kettle with one-half of the amount of formaldehyde needed. The reaction is allowed to take place, and the resin forms. After the removal of water, the resin is released through the bottom of the kettle onto a steel or concrete floor, as shown in Fig. 4-9. When cooled and hardened, the resin is ground for use in the manufacture of molding powders. In order to make the resin thermosetting, it is necessary to add more formaldehyde by mixing hexamethylenetetramine with the resin. "Hexa," as this compound is usually called, is a solid composed of ammonia and formaldehyde. The ammonia neutralizes the acid catalyst and, at the same time, the formaldehyde reacts with the resin.

While both the one-stage process and the two-stage process will produce resins that are almost identical, the two-stage process is easier to control because only one-half of the formaldehyde is used in the condensation reaction.

4-32. Mixing Ingredients for General-Purpose Molding Compounds.—General-purpose molding compounds, heat-resistant molding compounds, and medium-impact molding compounds are produced in the same manner. The resin, which has been ground to a fine powder, is placed in a spiral-blade mixer, and the filler selected to produce the type of compound to be made is added. The motor is turned on, and the revolving blades thoroughly mix the resin and the filler. The lubricants and the coloring matter are then added; and mixing is continued until a homogeneous mixture is obtained. A small sample is then removed and calender-rolled until all the ingredients have thoroughly fused. The sheet is taken from the rolls and is molded into a small button to check the



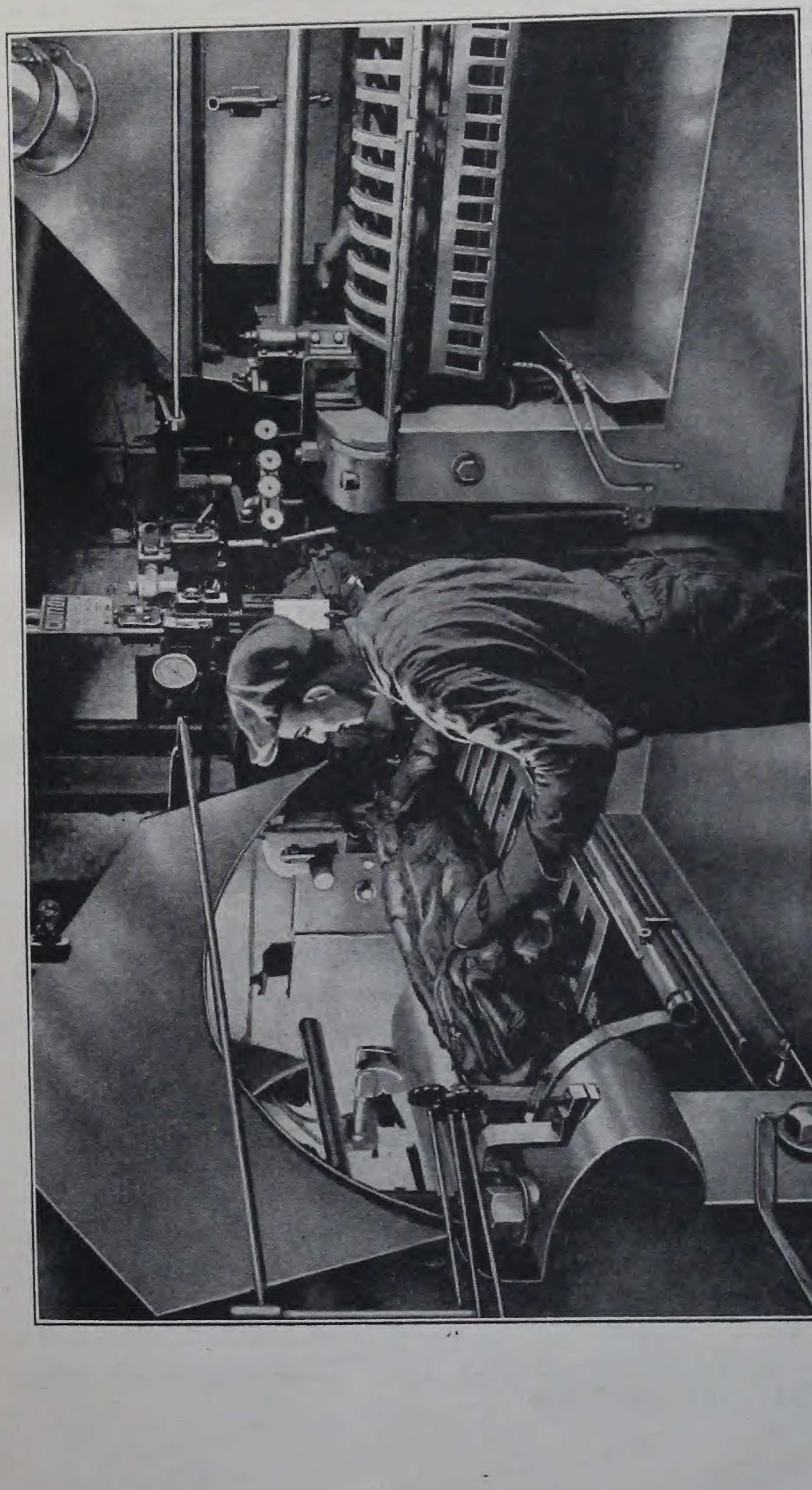
(Courtesy of the Monsanto Chemical Co.)

Fig. 4-9. Pouring Resin on Steel or Concrete Floor.

color of the material. If the color is not correct, additional coloring agents are added to the mixture, and the sampling process is repeated. When the color is finally correct, the material is ready for the production rolls.

The resin is tested before it is placed in the mixer. Any variation of the resin from the proper A-stage is adjusted in the formulation. If necessary, an accelerator or a retarder is added in the mixer. When the rolling process is started, the resin can be assumed to be properly developed within the A-stage.

4-33. Rolling of Molding Compounds.—The rolls for producing molding compounds are two large cylindrical steel rolls that are mounted horizontally and are revolved in opposite directions at different speeds. Such rolls are shown in Fig. 4-10. The ratio of the speeds of the two rolls is about 5 to 3, the front roll being



(Courtesy of Union Carbide and Carbon Corp.)

Fig. 4-10. Production Rolls for Blended Mixture of Resin, Filler, and Coloring Matter.

the faster. The back roll is mounted so that it can be moved until it either touches the front roll or is any desired distance away from the front roll. Both rolls are cored for steam and cold water. The back roll is heated to about 320° F, and the front roll to about 220° F. These temperatures must be maintained throughout the rolling operation.

If the rolls get too hot, enough cold water is circulated through them to bring the temperature back to the correct degree. If the rolls lose heat, more steam is circulated through them until the correct temperature is reached. At no time during the rolling must the operation be allowed to stop. The circulating of water or steam is done while the material is on the rolls.

A charge of material sufficient in weight to produce a sheet of the desired thickness is placed on the rolls. The usual thickness of a sheet is about $\frac{1}{4}$ inch, and the charge corresponding to that thickness weighs about 40 pounds. When the material comes in contact with the hot rolls, it forms a coating around the front roll. A knife, running the full length of the roll, is mounted directly in front of the front roll. By manipulation of the knife, the material can be cut away from the roll and placed again between the rolls. The material is thoroughly mixed by proper handling of this knife. Owing to the heat on the rolls, polymerization takes place during the rolling operation, which is continued until the resin is polymerized to the B-stage. The ability to determine when the B-stage has been reached is acquired with experience in the rolling operations. It has been found that a correct A-stage resin will reach the B-stage in a definite length of time under the proper temperature condition of the roll. The rolling operation is controlled by time. When the B-stage has been reached, the material is ready for removal from the rolls.

4-34. Removal of Material From Rolls.—A pan under the rolls catches any material that drops through at the start of the rolling operation. A conveyor belt under the pan is set in motion a few seconds before the material is ready to be removed from the rolls. The speed of the conveyor belt is the same as that of the front roll, so that the material is carried away at the rate at which it is removed from the roll. This arrangement is identical with that used for rolling shellac materials. The sheet remains on the conveyor belt until cooled.

4-35. Production of Phenolic Molding Powder.—Once the rolled material is cooled, it is ready for a grinding or crushing operation. There are many ways of carrying out this operation. Some manufacturers use an ordinary ice breaker, which is a rotating drum with spikes attached to it along tangents to the surface of the drum. Underneath the drum is a steel comb, the teeth of which are about $\frac{3}{4}$ inch apart. The material being hit by the spikes on the rotating drum is broken into small chips, which pass through the teeth of the comb onto another conveyor belt. A pulverizer at the other end of this conveyor belt breaks the chips into small granules. In this form the material is known as molding powder. It is advantageous to screen the molding powder in order to remove the particles that are too fine, as these "fines" cause trouble in the molding operation. A screen in the pulverizer usually controls the granulation of the powder, but some fines always result. The fines are blended in small amounts with the regular powder.

Another method of breaking up sheet stock is by whipping. In this process the sheet is actually lashed by leather strips mounted on a rotating shaft. As a rule the conveyor belt is boxed in, so that the material on the belt is somewhat confined during the lashing process and the small chips are prevented from scattering.

Many of the 40-pound sheets will be rolled of material that is intended to be of one particular type and color, but it is possible that there will be a variation between the sheets. It is therefore necessary to take all of the material from one batch and blend it. The blender is a machine of the same type that is used for the original mechanical mixing of the raw materials. The blended and screened material is the phenolic molding powder.

4-36. Applications of Phenolic Molding Compounds.—Phenolic molding compounds are used to manufacture such articles as buttons, handles, closures, radio cabinets, terminal blocks, electrical insulation parts, wall plates, camera cases, and industrial housings. The compounds are found under such trade names as Bakelite, Resinox, Durez, Indur, Makalot, and Durite.

4-37. Special Impact Molding Compounds.—Ordinary impact materials are manufactured in the same way as general-purpose materials, but certain applications that require greater shock resistance contain fabric or pieces of canvas as their filler. The

nature of the filler is such that it cannot be handled by the mixing and rolling processes. This method of manufacture has been tried, but the appearance of the molded article was not satisfactory, as pieces of cloth appeared on the surface of the article. The problem was to find a way to impregnate the filler so that in the molding process the resin, and not the filler, would show on the surface. Spraying is the method used to achieve this result.

The resin is the same as that used for general-purpose compounds. Instead of allowing the resin to cool and harden, however, it is dissolved in a mixture of alcohols and ketones. The coloring matter, which in this case is a soluble dyestuff, the lubricant, and the accelerator or retarder, if needed, are added to the resin solution and the mixture is thoroughly agitated. The filler is then thoroughly sprayed with the resinous solution. Low-temperature drying evaporates the solvents in the sprayed material. The resin-impregnated filler is the high-impact molding compound.

4-38. Ingredients of Cast Phenolics.—As the name indicates, cast phenolics are plastic materials that are formed by casting, not by molding. Unlike other phenolic materials, cast phenolics are 100 per cent resin. Fillers, accelerators, and plasticizers are not used in this type of compound. The resin is made by the same process that is used for other phenolic materials. Cast phenolics use an alkaline catalyst, and the chemistry of the reaction is similar to that involved in the Blumfeldt theory. When the resin reaction is complete and the water is distilled off, the resin is ready for casting.

If a colored resin is desired, the coloring agent is added in the kettle and is mixed thoroughly with the resin. Only soluble dyestuffs can be used. A water-soluble dyestuff can be used if it is added to the resin before the distillation. Mottles and grainings are possible in cast phenolics. Most grainings are accomplished by a simple process called rod dipping. In this process a glass rod is first dipped into a kettle of resin. As the rod is withdrawn, some resin will adhere to it. The rod with the adhering resin is then plunged into another kettle containing resin of a different color. By twisting and swirling the rod, the resin on the rod is mixed with that in the second kettle.

4-39. Molds for Cast Phenolics.—A lead mold for articles of cast resin is made by dipping a steel master form of one of the

articles to be cast into molten lead and removing it slowly. The lead adheres to the master form and takes the exact shape of the required mold. The lead is then carefully stripped from the master form. This form must have no undercuts, as they would make it impossible to remove the lead mold in one piece. Cast phenolics therefore find their main application in straight-draw or tapered articles, such as knife handles, fork handles, jewelry, brush backs, clock cases, and instrument dials. A large volume of the material is manufactured as rods and tubes that are subsequently sliced into thicknesses suitable for fabrication of articles. Bracelets, for instance, are usually made by first casting a tube about 2 feet long and then slicing the tube into about twenty-four ringlets. Each ringlet is worked on by hand or by a special routing machine, to produce the desired decorative effects.

4-40. Production of Cast Phenolics.—In the manufacture of cast phenolics, many individual lead molds are bound together to form a battery of molds. The liquid resin is poured slowly into the molds while the resin is hot, so that all air bubbles in the liquid are brought to the surface. The molds are then given a heat treatment similar to that for cold-molded plastics. The battery is placed in an oven and the temperature is slowly raised until it reaches 176° F. The heating period takes from 3 to 5 days, the exact period depending on the amount of material required for each article. At the end of the heat-treating period, the molds are removed from the oven and are turned on end. Slight pressure from a pneumatic hammer will knock the article from the mold. Taper on a casting greatly facilitates ejection from the mold.

When the resin is poured into the mold, it is in the A-stage. It completes both the B-stage and the C-stage during the oven treatment. At the end of the first or second day in the oven, the resin is partially soluble and partially fusible. This is the B-stage. When the articles are removed from the oven, they are insoluble and infusible. This is the C-stage. Because the cast resins are placed in the oven at the A-stage and are removed at the C-stage, they are thought of as having no definite B-stage. Technically, however, the resins pass through the B-stage during the first portion of the oven treatment.

Cast phenolics are usually placed on the market under the names of Bakelite Cast Resinoid, Catalin, and Marblette.

4-41. Phenolic Resin Board and Blanks.—In certain molding applications of the high-impact type, it is advantageous to have the article in a preshaped form. Instrument cases such as those used for voltmeters and ammeters are good examples of preshaped moldings. The case usually has a metal frame that is augmented by phenolic material. Use of ordinary high-impact phenolic molding powder presents difficulties in the molding operation. The strength of the completed article is not uniform, owing to the unevenness of the flow of material. Unevenness of flow is aptly demonstrated when one observes a stream of water flowing around an obstacle which stands above the water level in the middle of the stream. The water approaches the obstacle in a uniform manner. When it meets the obstacle, the stream divides and passes on both sides of the obstacle. After the barrier has been passed, the water swirls and the parts join again to form a smoothly flowing stream.

Molding materials sometimes have to be molded around a core or a large pin. The material has to be divided and then reunited to form a single unit. While the material is flowing, it is polymerizing, which means that it is getting harder. Where the application is difficult, the material sometimes cannot flow together and flux completely. If this happens, the joining point is a weak spot in the molding, and the article is apt to break or crack when put into use. One method of overcoming difficulties of this nature is to have the material already joined so that no flow is needed. Phenolic boards and blanks accomplish this.

In making phenolic boards and phenolic blanks, ordinary sheets of cardboard are dipped into tanks of hot phenolic resin. Duration of impregnation will depend on the thickness of the cardboard. The impregnated sheets are then put through a low-temperature drying operation, which evaporates the excess solvents that were used to dissolve the resin. The sheet is then ready for the stamping operation, and the stamped blanks in the form of sheets, slugs, and punched shapes are used in the molding procedure instead of molding powder.

Under the trade names of Bakelite Rogers Board, and Bakelite Rogers Blanks, the material is used in the manufacture of bobbin heads, scabbards, helmets, and bayonets.

4-42. Phenolic Pulp Products.—Phenolic pulp materials find their main use in high-impact applications where, owing to com-

plicated shapes, phenolic board or blanks or high-impact molding materials cannot be used. The mixture of liquid resin, filler, and the other ingredients necessary in a molding compound is placed in a suction device, which is a crude form of the article to be molded. The suction will preshape, in a crude way, the article to be molded. The *preform*, as it is called, is put through a partial drying operation, which evaporates the solvents from the liquid without polymerizing the resin. When the preform is dry, it is ready for use in the molding operation. Since the preform was made to conform to the shape of the article to be molded, there is practically no flow of the material. Only complete polymerization of the resin is needed to produce the article.

Trays, license plates, machine housings for office equipment, etc. are usually produced from phenolic pulp products. Commercially they are known as Kys-ite.

4-43. Phenolic Asbestos Composition.—Materials designated as phenolic asbestos composition should not be confused with the heat-resistant phenolic material that uses asbestos as its filler. Phenolic asbestos composition refers specifically to a commercial material known as Haveg. Haveg, unlike most molding materials, does not require a definite mold or the usual molding temperature. It is used mainly for the construction of tanks and digesters because of its excellent resistance to acids. The material is made by mixing liquid phenolic resin with a special acid-treated asbestos. The resultant mix is similar to putty. It is usually stuffed into wooden molds and allowed to harden.

4-44. Phenolic Transparent Molding Compounds.—Transparent molding materials contain no filler. The resin in compounds of this type is made in the same way as that for other phenolic molding compounds, the two-stage process being the one most frequently used. The resin is mechanically mixed with hexamethylenetetramine in conjunction with lubricant. The powdery mixture is placed in a U-blade or Sigma-blade mixer. In this instance, the blades are heated and the entire mixer is jacketed for steam and cold water. The mixer is started and the heat soon softens the phenolic resin. At about the time at which softening starts, the coloring matter, previously dissolved in alcohol, is added.

The material reacts chemically. The hexa breaks down to form ammonia and formaldehyde. When the entire mass starts to

granulate, cold water is fed through the blades and jacket, and the material is removed. After cooling, it is ground. The resultant powder is the molding compound. Hexa is not the only material that can be used to supply the needed formaldehyde to complete the second stage of the process. Ordinary formaldehyde, when polymerized, yields a white solid called paraform, which is entirely suitable as the source of formaldehyde for the second stage.

Transparent phenolics, under the trade name of Bakelite Transparent, are used in the manufacture of articles of jewelry, dials, and name plates.

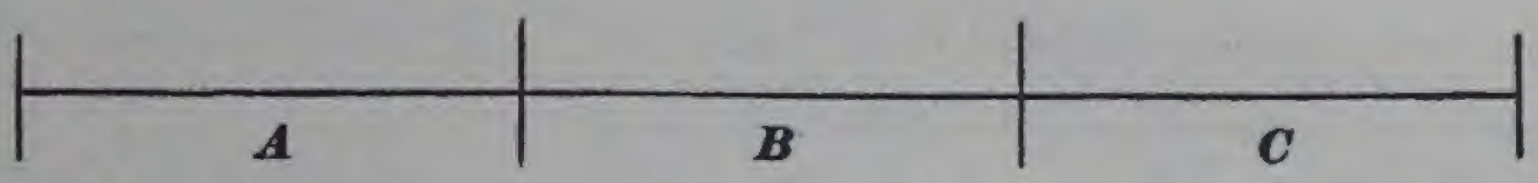


Fig. 4-11. Graphic Representation of Normal A-Stage, B-Stage, and C-Stage Resins.

The hot-kneading process for transparent phenolics is comparable to the hot-rolling process for regular phenolic molding compounds. The temperature and length of time in the mixer are very important and must be closely watched. Since these plastics are transparent, the moisture content is also very important. If too much moisture is present, molded articles will be cloudy. Because of the inherent yellow color of phenol, no clear water-white phenolic is possible. The best that can be accomplished is to produce an amber. Unsuccessful attempts have been made to add a small percentage of blue dyestuff to counteract the yellowness.

4-45. Normal Three-Stage Development of Resin.—All types of phenolic materials are based on phenolic resin made by a condensation reaction. The type of filler will depend on the use to which the material is to be put. Where transparency is desired, no filler is used. The addition of accelerators and retarders depends entirely on the A-stage of the resin. The conditions of temperature and time in the B-stage depend on the formula and the flow desired.

The A-stage and B-stage diagrams may now be studied with reference to the C-stage, as graphically illustrated in Fig. 4-11. The resin at the A-stage is suitable for use in the B-stage without accelerator or retarder. The B-stage has been carried out under regular conditions. The C-stage, or molding stage, is normal. The length of time required for the resin to polymerize is correct.

It is important to remember that the correct condition of the C-stage is not interpreted to mean the time required to mold an

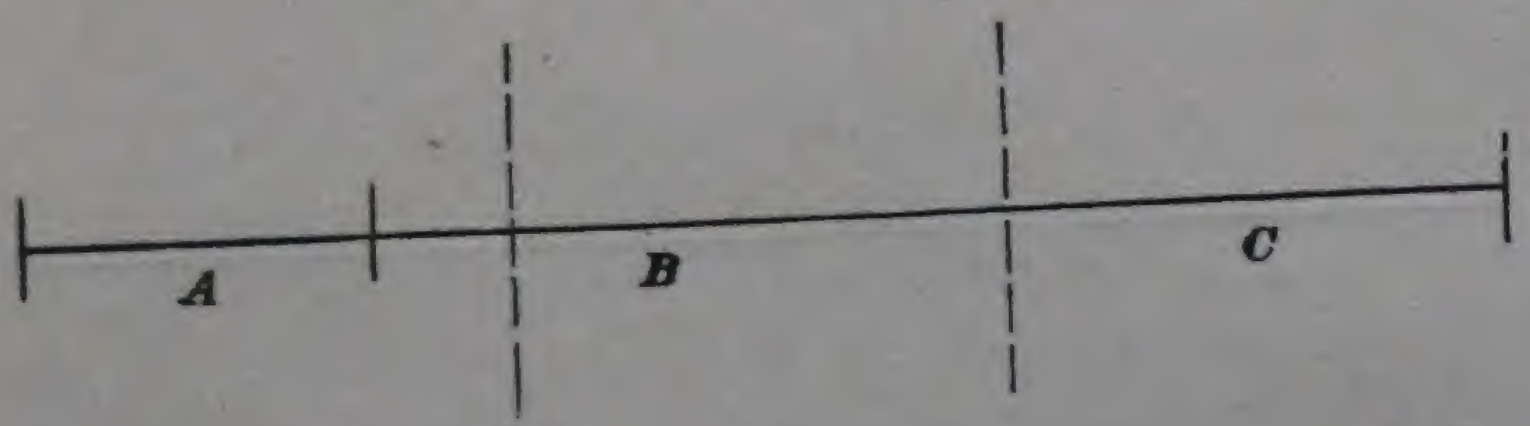


Fig. 4-12. Condition of Slow Resin With and Without B-Stage Adjustment.

article. The time required for molding depends on several factors other than the condition of the resin. As long as the A-stage and the B-stage are correct, the C-stage will follow by using normal procedure. A button requires about 1 minute to mold; a telephone receiver requires 4 minutes to mold. The C-stage is not to be thought of in terms of time, such as 1 minute for the button and 4 minutes for the receiver. These objects have different molding time because of their difference in weight and complexity of shape. The C-stage is the complete polymerization of the resin. The same resin base can be used to produce both the button and the telephone receiver. Moreover, the polymerization rate is the same in both cases, even though the periods of time required for molding are different.

4-46. Variations in Resin Development.—In diagram (*a*) in Fig. 4-12 the resin reaction has not advanced far enough, and it is necessary to add an accelerator. The combination of the A-stage and the B-stage is correct, so that the C-stage compares favorably with the norm, which is indicated by dotted lines.

In the case of diagram (*b*) of Fig. 4-12 the resin is slow. No accelerator has been added to the formula. The manufacture goes through the standard procedure, or a normal B-stage; and the C-stage must make up for the deficiency. It will, therefore, take longer for the resin to polymerize than under normal conditions.

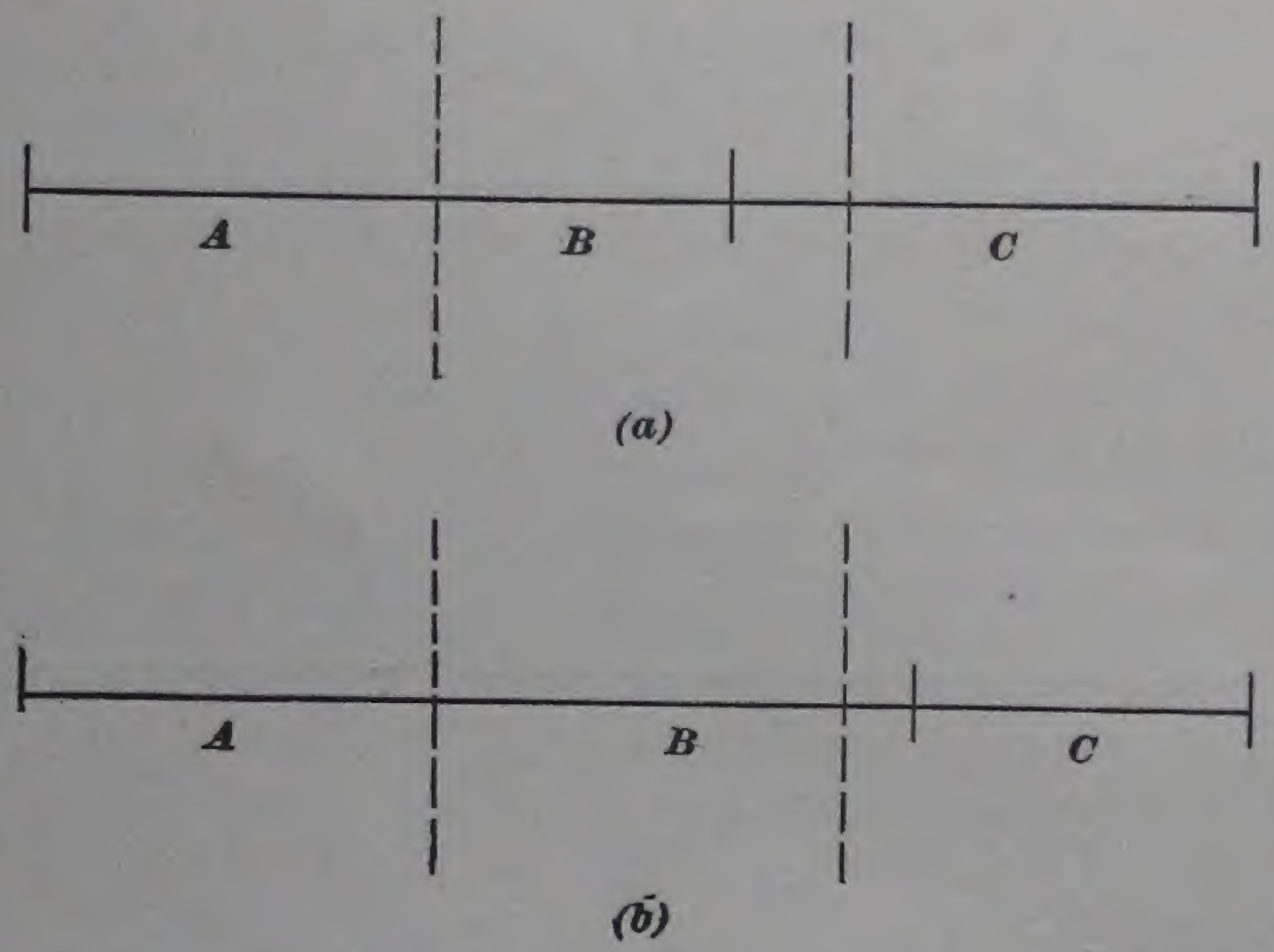


Fig. 4-13. Condition of Resin With a Shortened B-Stage and With a Fast B-Stage.

This condition will result in a longer C-stage. In addition to the regular molding period, time must be allowed for this extra polymerization. Since the molding operation involves labor, it is the most costly.

A correct resin development with a shortened B-stage is illustrated in diagram (*a*) in Fig. 4-13. Either the rolling time was not sufficiently long or the temperatures were too low. The C-stage, as compared to the norm, is too long. The same condition arose when the resin was slow and the B-stage was normal, as shown in diagram (*b*) in Fig. 4-12.

The effect of a fast B-stage is illustrated in diagram (*b*) in Fig. 4-13. In this instance the resin is normal. Despite this fact, accelerator has been added. The result is that the material has polymerized too far and the C-stage is abnormally short. Apparently this condition should prove an advantage, but it usually results in a disadvantage. Molding compounds of the foregoing type are usually fully cured before the material has flowed and filled out the article. An unfilled article is a reject, and so the material, as well as the labor applied, is lost.

The C-stage is always predetermined. The B-stage is the "fixer" stage. The complete success of a molding compound depends entirely on the B-stage.

Phenol Furfural

4-47. Chemistry of Resin Formation.—Phenol-furfural resins, which are condensation products of the reaction between phenol and furfuraldehyde, are thermosetting plastics that have the same stage developments as phenol formaldehydes. The structure of furfuraldehyde, or furfural as it is more commonly known, is as shown in Fig. 4-14. The reaction between furfural and phenol or

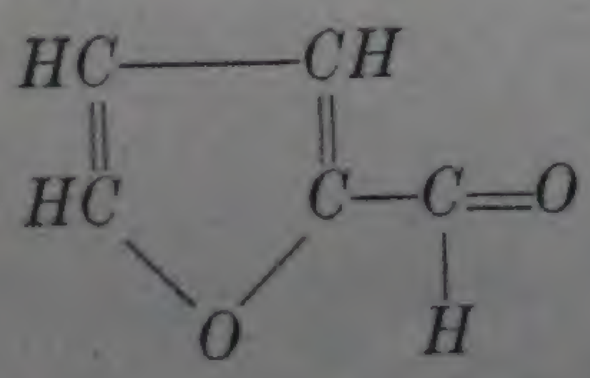


Fig. 4-14. Structure of Furfural.

cresylic acid is a typical condensation reaction, a chain-structure resin being formed with the usual elimination of water, as indicated in Fig. 4-15.

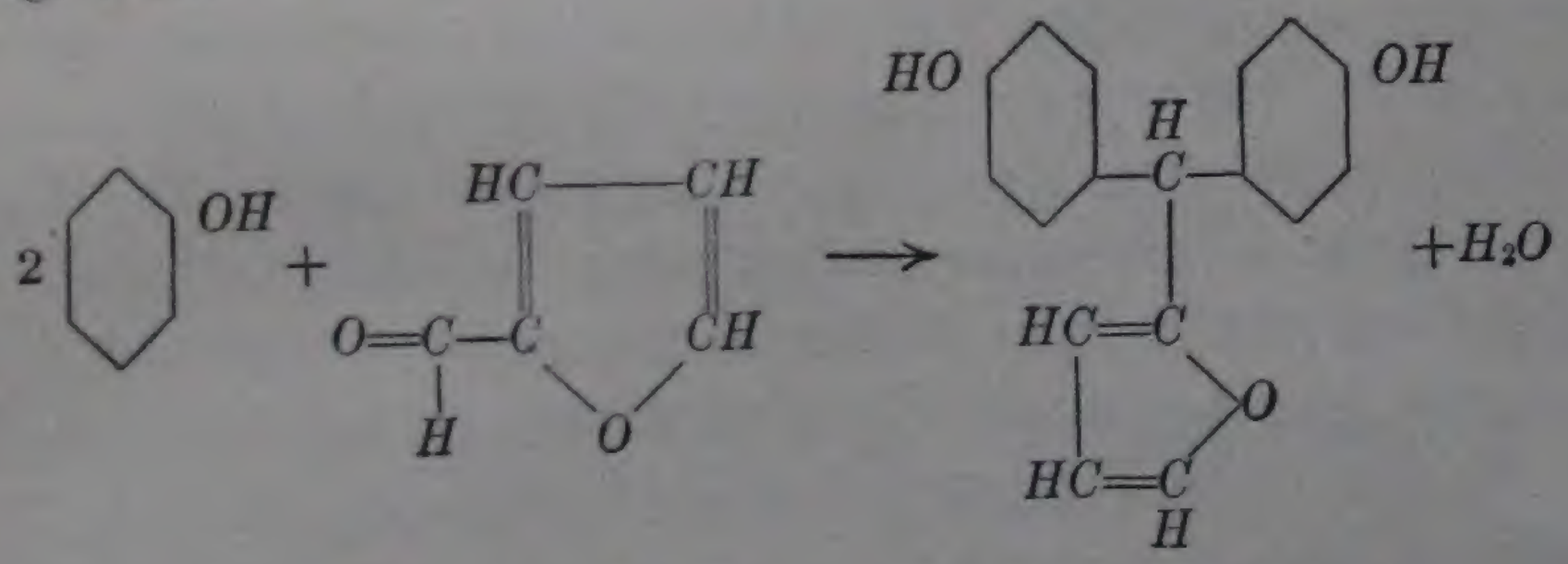


Fig. 4-15. Reaction Between Furfural and Phenol.

The equation represented in Fig. 4-16 shows the polymerization that takes place during the processing and molding stages.

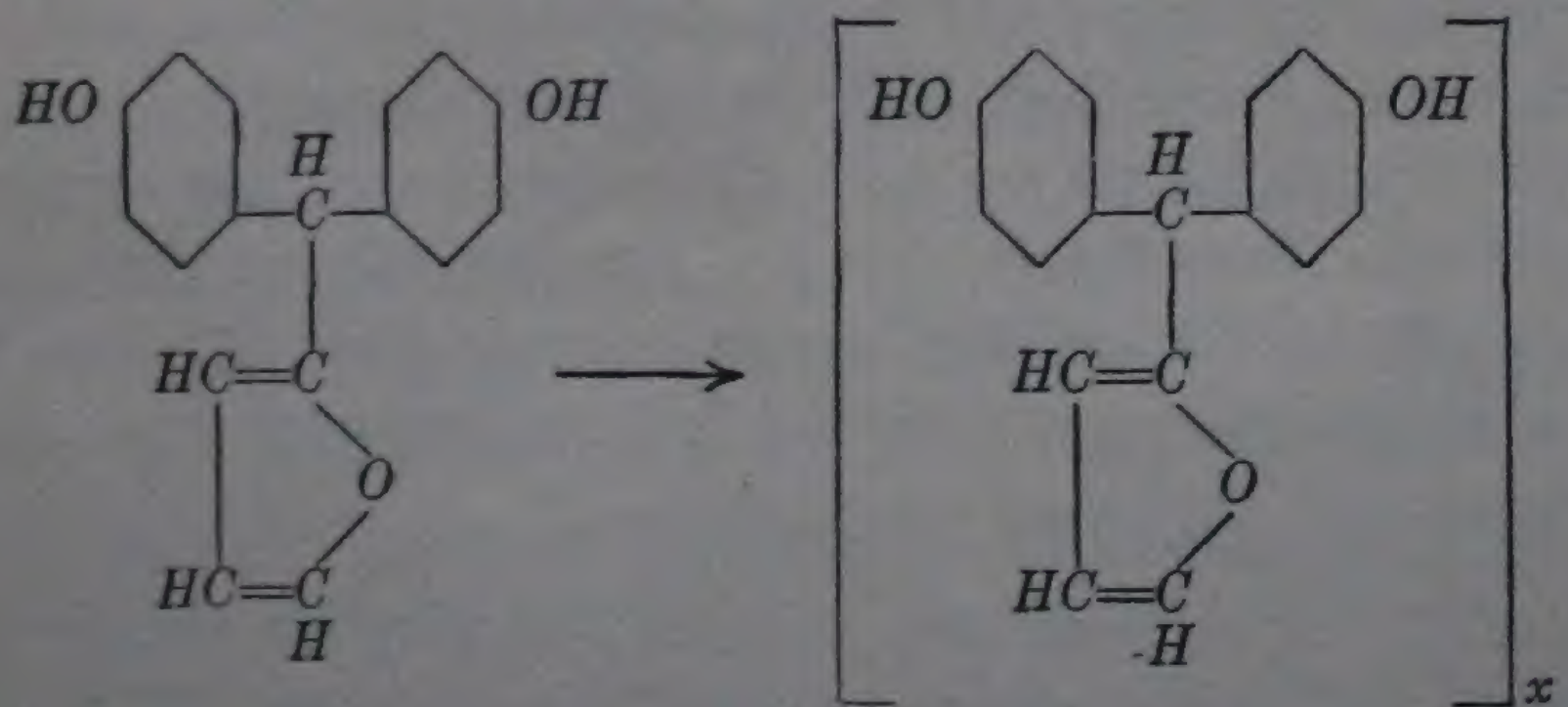


Fig. 4-16. Polymerization of Phenol Furfural.

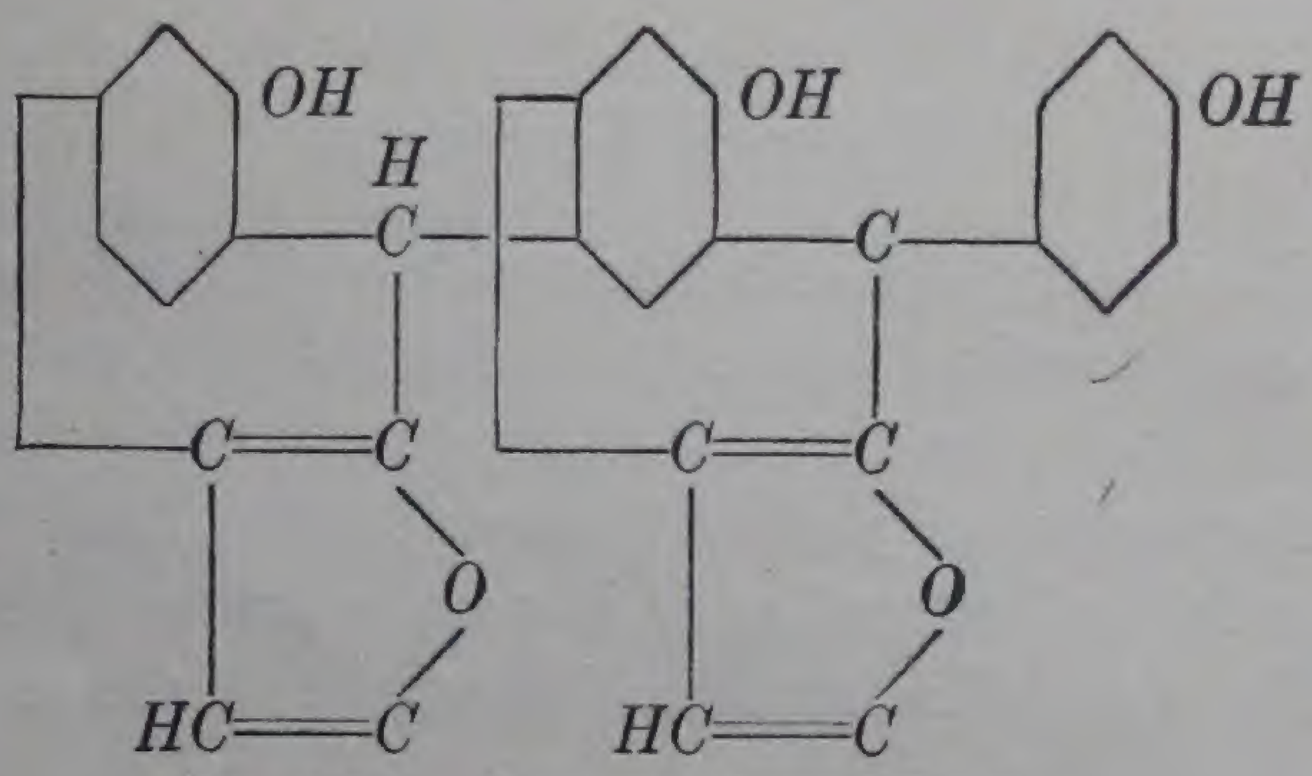


Fig. 4-17. Construction of Resite.

During these stages the furan ring, with its double bonds, plays the important part, insuring thorough cross-linkage. The resite, or C-stage resin, may be pictured in many ways, one of which is as shown in Fig. 4-17.

4-48. Raw Materials.—Because it is obtained from agricultural waste products, notably oat hulls and corn cobs, furfural is one of the cheapest aldehydes. To prepare furfural industrially, corn cobs or oat hulls are digested in a dilute acid solution, and the mixture is heated under pressure. The carbohydrate material hydrolyzes to form a lower molecular sugar known as pentose, which undergoes internal condensation to form furfural. The furfural is volatilized and collected in a pure form by passing steam through the digested mass. When relatively pure, furfural boils at 161.7° C, has a specific gravity of 1.16, and becomes brown on exposure to air.

The production of phenol was discussed in connection with the phenol-formaldehyde resins.

4-49. Manufacture.—The procedures used for the preparation of phenol-furfural compounds are identical with those used in the production of phenol formaldehydes. When the condensation resin has been thoroughly mixed with all the necessary ingredients, it is calendered to form sheets that are ground into molding powder. The methods for controlling flow and cure in phenol-formaldehyde compounds are also used with the furfural compounds.

4-50. Characteristics of Furfural Resins.—The outstanding characteristic of furfural resins is their ability to remain plastic for several hours if the temperature is kept below 325° F. It is thought that the furan ring is responsible for this behavior. Owing

to this plasticity, the compounding stage is less critical than for the formaldehyde resins. The fact that the compound will remain plastic as long as the rolling temperatures are below 325° F has led to a general theory that the furfurals do not pass through the customary three stages. It is thought that the A-stage and the B-stage together are a single phase of resin transformation. In general practice, however, the furfurals are treated as regular three-stage products. If necessary, an accelerator or a retarder is added in the processing, or B-stage, to bring the resin to a normal condition. This addition will affect the cure in the final molding process, just as it does for the phenol-formaldehyde products.

At temperatures above 325° F the furfurals lose their plasticity and rapidly polymerize to the insoluble and infusible state. As compared with the formaldehyde resins, the furfurals are much freer flowing. For this reason they are easier to mold into long-draw and large-volume articles.

4-51. Formulation.—A typical formula for a furfural molding compound is as follows:

	Per Cent
Binder (synthetic resin)	44
Filler (wood flour)	54
Lubricant (calcium stearate)	.5
Color (pigment or dye)	1.5

Accelerating and retarding agents are added to the mix as needed, but seldom are they added in amounts greater than 1 per cent.

4-52. Types and Applications.—The furfurals are produced in four general types, namely, general purpose, impact, electrical, and special duty. To impart the special property desired, the same ingredients discussed in the phenol-formaldehyde group are used. Wood flour is the most commonly used filler for the general-purpose compounds. For good impact strength, together with mechanical strength and shock resistance, the use of linen and canvas scraps is recommended.

Furfural molding compounds can be fashioned by compression, injection, or transfer molding. Furfural resins in the liquid state or in the powdered form are used for impregnating and laminating plastics and as varnishes and lacquers. Articles such as grinding wheels, buttons, wiring devices, wall plates, plugs, and munition parts are marketed as Durite.

Chapter Five

Other Thermosetting Plastics

Casein

5-1. Complexity of Proteins.—Casein is classified as a borderline thermosetting material of the protein type. Proteins are probably the most complex organic compounds with which the chemist must deal. Casein is one of the more complicated members of the protein family. The casein molecule is very large, with molecular weight determinations varying between 12,000 and 200,000. The exact chemical structure of casein is not known. Ordinary decomposition of protein matter yields a wide variety of amino acids. An amino acid is a compound that contains both an amino and a carboxyl radical in its structure.

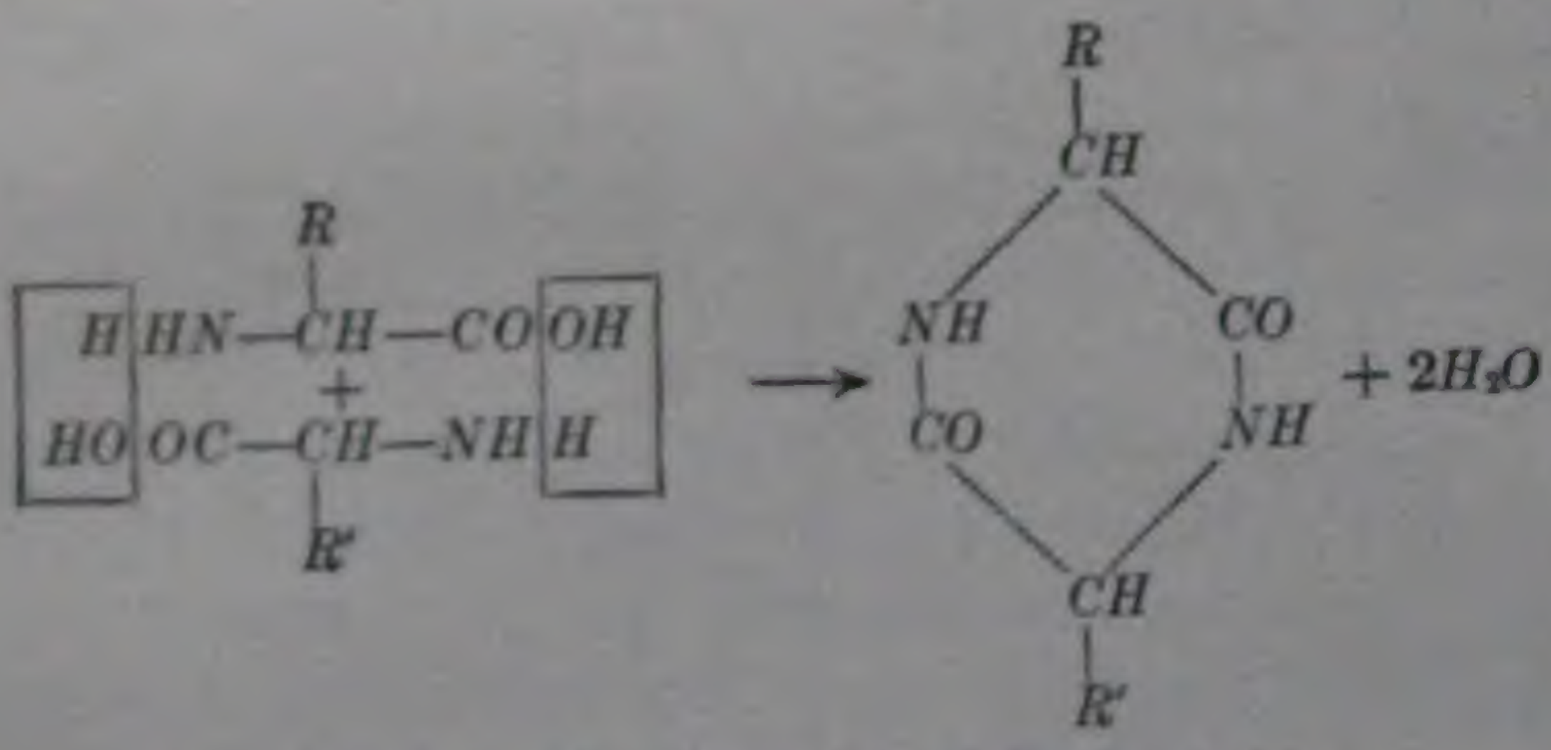


Fig. 5-1. Condensation of Amino Acids.

5-2. Theory of Linkages.—As early as 1900, Emil Fischer had definite views on how the proteins were structurally connected. His theory was that amino acids condensed with the elimination of water in the manner shown in Fig. 5-1. Fischer contended that the acids were joined together through the peptide linkage, *—NH—CO—*. X-ray studies have since confirmed the presence of this structure in casein.

Casein does not undergo polymerization. The large molecule consists of many cross-linked, straight-chain amino acids. Let the following formulas represent five typical amino acids:

$$RCH(NH_2)COOH$$
$$R_1CH(NH_2)COOH$$
$$R_2CH(NH_2)COOH$$
$$R_3CH(NH_2)COOH$$
$$R_4CH(NH_2)COOH$$

In a cross-linked protein molecule consisting of the foregoing acids, the structure would be as shown in Fig. 5-2, in which the amino

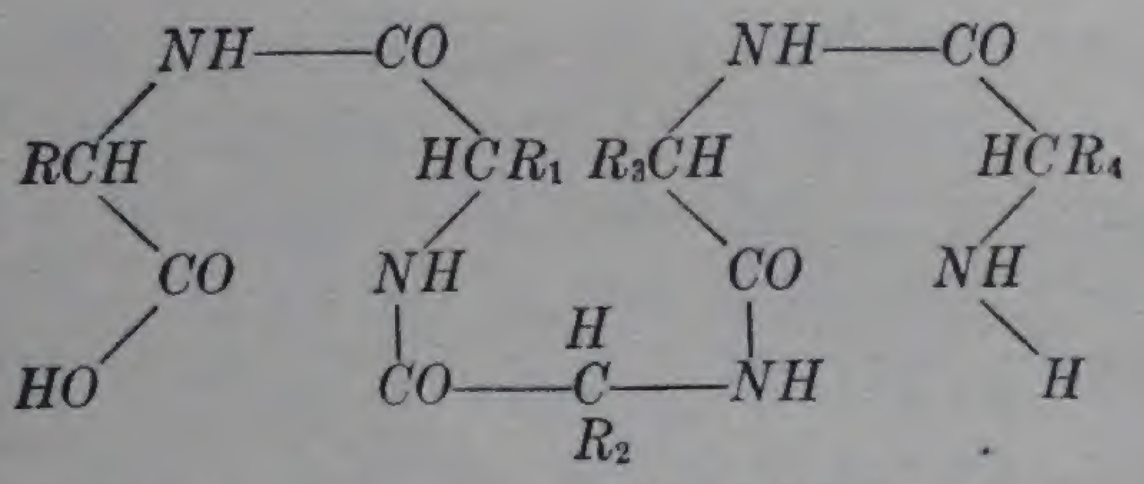


Fig. 5-2. Structure of Protein Molecule.

group of one molecule joins with the carboxyl group of an adjacent molecule.

The ends of the molecule are positions at which other amino acids may join. The size and kind of linking in a protein will depend on the type and number of amino acids present in that protein. So far, twenty-six different amino acids have been isolated from casein.

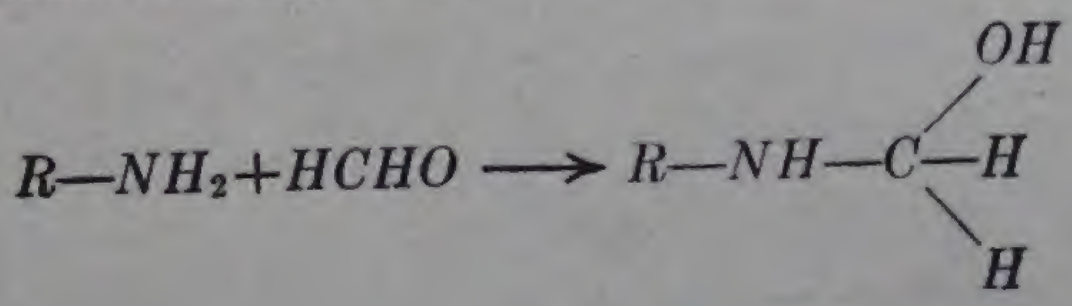
5-3. Casein-Formaldehyde Reaction.—Casein is a borderline compound. In its initial stages as a plastic material it is thermoplastic, but subsequent treatment of the material in a formaldehyde bath gives it the properties of a thermosetting material. The chemistry of the casein-formaldehyde reaction still remains a debatable point. For a long while the Blum theory was held in favor. This theory holds that free amino groups actually condensed with the formaldehyde with the elimination of water as follows:

$$R—NH_2+HCHO \longrightarrow R—N=CH_2+H_2O$$

In the foregoing reactions, R represents casein.

Research work on the amino acids lycine and histidine definitely proves that the methylene linkage $R—N=CH_2$ is not present. Since these acids are present in casein to the extent of 10 per cent, it is reasonable to believe that the Blum theory is not entirely correct.

Another theory has been advanced which advocates the aldehyde-ammonia linkage represented as follows:



In any case, much more will have to be known about the structure of the casein molecule before the actual linkage of the formaldehyde reaction can be determined.

5-4. Methods of Preparing Casein.—Casein is obtained from skim milk. The curd that forms in milk that has soured is casein. In production, casein is made by treating skim milk with sulfuric acid or hydrochloric acid. The milk is heated to 120° F and the acid is added. About $2\frac{1}{2}$ pints of commercial acid diluted with an equal volume of water is required per 1,000 pounds of milk. Constant agitation while adding the acid insures good separation of the curd from water. The water and any excess acid is removed, and the curd remaining is washed thoroughly with warm water. Washing continues until the curd is neutral to litmus. Because acid is used in its production, casein of this type is called acid casein.

Enzyme fermentation is another method used to prepare casein. Enzymes are substances that are produced by minute living organisms and that cause chemical decomposition. In the production of casein, the enzyme called *rennet* is used. Skim milk is heated to about 96° F and the enzyme, which has been previously dissolved in water, is added. The amount of rennet will depend on the condition of the skim milk. The more acid there is in the milk, the less rennet is required. About 100 milliliters of rennet per 1,000 pounds of milk is the correct proportion under ordinary circumstances. Precipitation of the curd starts almost immediately on the addition of rennet. The mixture is heated to 150° F in order to insure good separation of curd and water. When separation is complete, the water is drawn off and the curd is thoroughly washed with clean, warm water. Rennet casein is the type that is used mainly in the manufacture of plastics. A flow chart for the production of casein plastics is shown in Fig. 5-3.

5-5. Other Ingredients.—There are many plasticizers for casein. Most prominent are the fatty oils such as Turkey red, aniline, and sulfonated castor oil. Glycerol has also been success-

fully adopted. Most of these plasticizers are synthetic or distilled products.

Protein materials have always been known as excellent color retainers. This color retention, plus the fact that rennet casein is a pale straw color, enables all shades of all colors to be made. Acid dyestuffs have been found to be the best for casein materials. Most dyestuffs used for casein are of the synthetic type.

Casein is thermoplastic in its initial stages; so it needs no accelerator or retarder. Fillers are not necessary in the manufacture of the molding compound. Casein, in this respect, is like cellulose.

5-6. Preparation of Slugs.—Casein materials are used mainly for buttons, buckles, and similar articles. This may be explained by the fact that newer materials with better molding and physical properties are available for most plastic applications. As a rule, casein is not produced as a molding compound but comes in the form of rods or tubes. The rods are subsequently placed in automatic screw machines which turn out preformed buttons or slugs similar to buttons. Molding machines convert the slugs into the final buttons.

To produce slugs, dry powdered rennet casein is first placed in a mixer of the kneading type. Ordinary dough mixers such as a baker would use are satisfactory. Enough water is added so that, when thoroughly mixed with the casein, it produces a stiff paste. Suitable plasticizers and dyestuffs are added to the churning mixture, and the kneading is continued until homogeneity is obtained. The resultant plastic is placed in an extruder that produces rods or tubes. These are further processed in automatic screw or slicer machines into slugs that will eventually be made into buttons. The material at this point is still thermoplastic.

5-7. Formaldehyde Treatment.—After the buttons have been manufactured by machining or molding, they must be hardened in a 5% formaldehyde solution. The length of time in the bath depends entirely on the thickness of the button. For ordinary decorative buttons, approximately 2 days is required. When the buttons are removed, the casein is thermosetting. The use of 2 per cent of alum in the original mixture, as practiced by some manufacturers, reduces the time required in the formaldehyde bath.

The formaldehyde bath is the most critical part of the casein process. Casein, because of its affinity for water, is not suitable

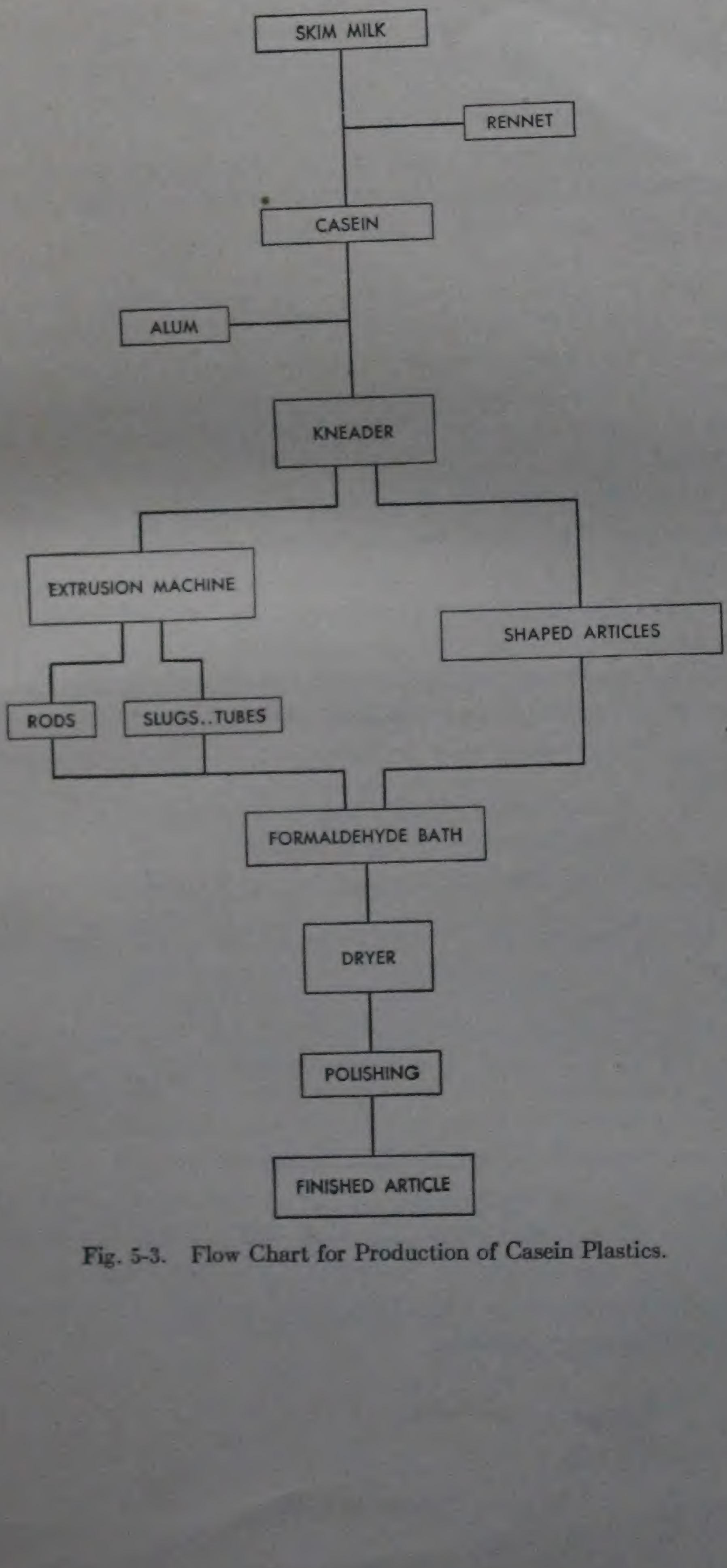


Fig. 5-3. Flow Chart for Production of Casein Plastics.

as a molded article in the thermoplastic state. An unhardened casein object will absorb water and will warp. Extreme weather changes will cause cracking. The hardening must be uniform in order to prevent warpage or shrinkage later on. The depth of hardness must be sufficient to prevent the material from absorbing too much moisture. If the hardening takes place too quickly, internal strains will be produced.

5-8. Functions of Ingredients.—In casein plastics, the casein itself acts as both binder and filler. The water used to soften the casein in the primary mixing process may be thought of as a plasticizer. It is not sufficient, however, and additional plasticizer such as a fatty oil must be used. The plasticizer also acts as a lubricant.

Throughout the material manufacturing stage, casein is thermoplastic; therefore, no accelerator or retarder is actually needed. The alum might be thought of as an accelerator, since it does speed the curing reaction of casein and formaldehyde.

5-9. Casein and Its Applications.—A typical formula for the manufacture of casein as a moldable material is as follows:

	Per Cent
Binder and Filler (rennet casein)	90
Plasticizer (water and glycerin)	8
Color (acid dye)	2

Casein is obtainable in the shapes of sneets, rods, tubes, disks, and slabs. It may be handled by compression molding, by extrusion molding, by chemical hardening, or by machining extruded parts. Under the trade names of Galorn and Ameroid, it is commercially marketed in the form of buttons, buckles, beads, and game counters.

Urea Formaldehyde

5-10. General Considerations.—The urea resins, like the phenolics, are thermosetting, and they cure as readily as the phenolics. They are superior to the phenolics, however, in that they are completely colorless, a fact that affords greater variety of color by dyeing and pigmentation.

5-11. Chemistry of A-Stage.—When reacted with formaldehyde under suitable conditions of temperature and pressure, and in the presence of a catalyst, urea probably forms monomethylol urea and dimethylol urea according to the equations shown in Fig. 5-4.

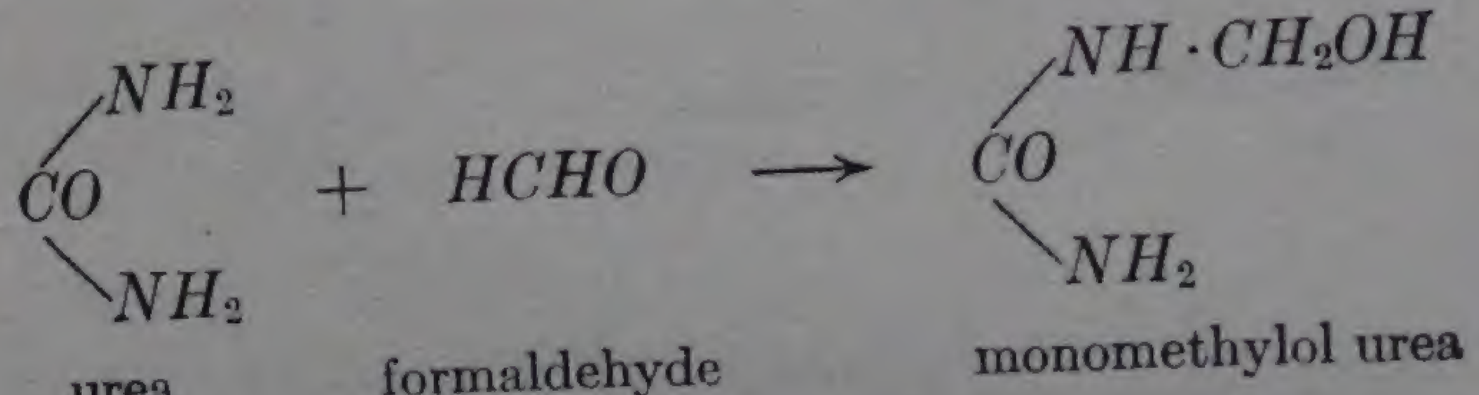


Fig. 5-4. Reactions of Formaldehyde With Urea.

5-12. C-Stage.—Monomethylol urea or dimethylol urea can condense in an acid or alkaline medium to produce methylene urea or dimethylene urea. The latter compounds have the power to attach to one another in open-chain or closed-chain fashion, forming giant molecules referred to as resinous material. The equations shown in Fig. 5-5 attempt to explain the reactions involved in the formation of urea resins.

5-13. Hydrogen-Ion Concentration.—The most important factor in the reaction of ureas with formaldehyde is the condition of the solution with respect to acidity or alkalinity. Two distinct chemical stages must be considered in the production of urea resins. In order to keep the resin in the A-stage, the solution must be alkaline. The *p*H of formalin is about 3, and this is so acid that the reacting solution must be adjusted. This adjustment is made by using an alkaline catalyst such as sodium hydroxide or barium hydroxide. The curing of the material in the subsequent molding operations is very slow if it is alkaline; so an acid accelerator is added in the compounding stage. Salts such as ammonium chloride tend to give acids on heating. The acid formed by the accelerator in the molding stage makes the compound acid and allows rapid cure. The chemistry involved in the cure is the dehydration of the

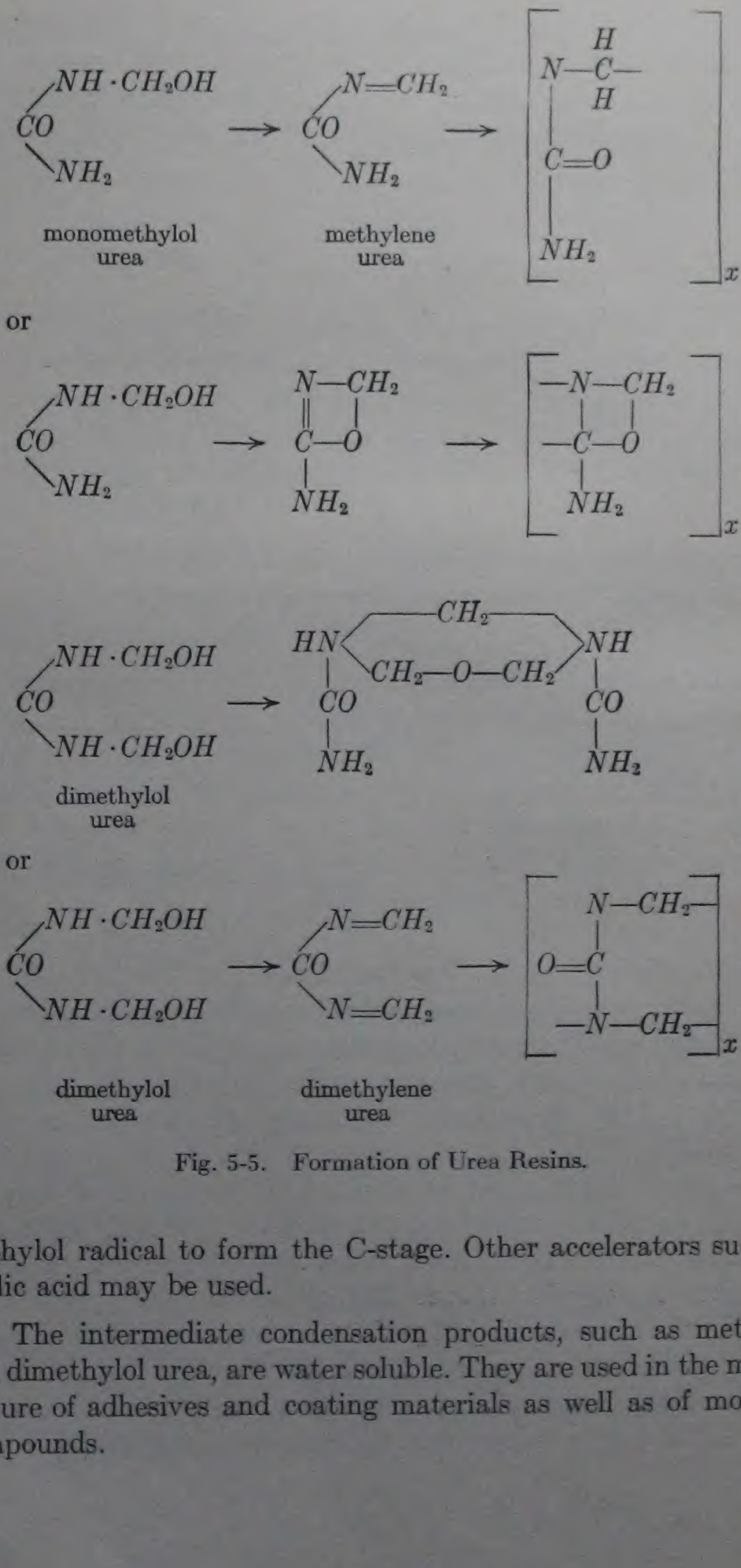


Fig. 5-5. Formation of Urea Resins.

methylol radical to form the C-stage. Other accelerators such as oxalic acid may be used.

The intermediate condensation products, such as methylol and dimethylol urea, are water soluble. They are used in the manufacture of adhesives and coating materials as well as of molding compounds.

5-14. Production of Formaldehyde.—Various methods for the production of formaldehyde are in use. Suffice it to say that formaldehyde results from the direct oxidation of methyl alcohol or the direct union of carbon-monoxide gas and hydrogen gas. Extreme care in the handling of formalin solution is necessary because the fumes given off are toxic. Since formaldehyde readily attacks certain metals, materials that come in contact with it must be formaldehyde-resistant.

5-15. Preparation of Urea.—Urea is a white crystalline solid which melts at 132° C. It dissolves readily in water. Commercially, this product can be synthetically made at low cost by combining ammonia gas with carbon dioxide. Ammonia gas is synthesized by the direct union of nitrogen and hydrogen or is obtained as a by-product of coal distillation. Carbon dioxide is obtained as a by-product of refinery gases, fermentation processes, or complete combustion of coal.

In the synthesis of urea, which involves the use of high pressures and special steels, ammonia and carbon dioxide are first compressed. Then, by heating the gases to 120° C and allowing them to stand in a specially constructed reactor, the reactions shown in Fig. 5-6 take place. To separate the urea as a granular material

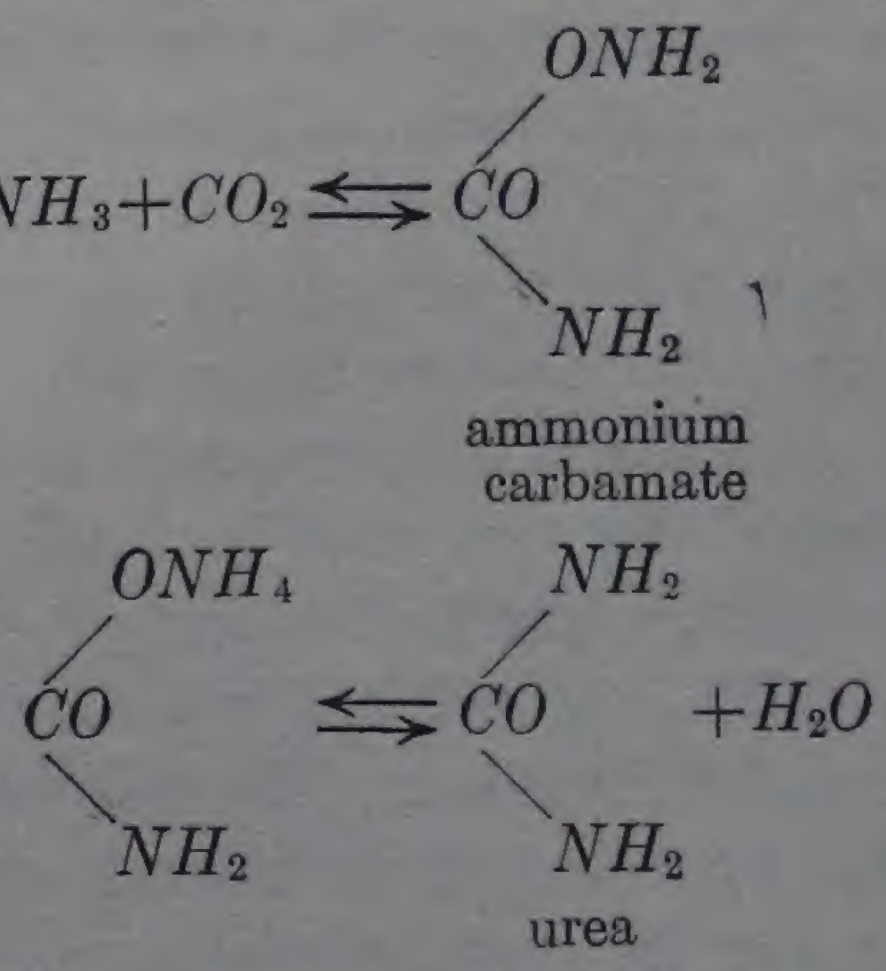


Fig. 5-6. Formation of Urea.

from its water solution, the material from the reactor is sprayed into a chamber through which hot air flows. The hot gases evaporate the water, leaving the urea in a dry, solid state.

5-16. Preparation of Urea Resin.—The correct ratio of urea to formaldehyde to produce good cross-linkage in the resin is

approximately 1 to $1\frac{1}{2}$ by molecular weight. Urea has a molecular weight of 60 and formaldehyde, 30; so a correct ratio would be 60 pounds of urea to 45 pounds of formaldehyde. Since the formaldehyde is commercially supplied as a 40% solution, the weight of formaldehyde needed must be multiplied by 2.5 to get the weight of 40% solution required. Thus, to obtain 45 pounds of formaldehyde, it would be necessary to use 112.5 pounds of a 40% solution of formaldehyde.

Because of the corrosive action of urea-formaldehyde reactions, chromium-plated or monel equipment must be used. A jacketed kettle similar to the phenolic-condensation kettle is charged with the correct amounts of urea and formaldehyde. The *p*H of the solution is adjusted by the addition of an alkaline catalyst. The solution is allowed to stand for about 2 hours, the temperature being maintained at 20° C. During this time the initial condensation reaction forms the intermediate methylol and dimethylol resins, or A-stage resins, which are soluble and fusible. When the correct A-stage is reached, cold water is run through the jacket of the kettle to prevent any further reaction.

5-17. Removal of Excess Materials.—The volume of water formed by the condensation plus the water in the original formalin mixture is too great, and some of it must be removed. Some unreacted formaldehyde is recovered for the sake of economy. Vacuum distillation is employed to remove these excess materials. By using a vacuum, distillation takes place at a much lower temperature than at atmospheric pressure with the result, in this case, that the status of the urea resin is unaffected. Enough water is left in the mixture to enable the resin to be poured readily. Since the urea materials are produced in a variety of pastel shades, contamination is strictly forbidden. The dissolved resin is obtained clear and colorless by filtering to remove any foreign matter. This resin solution can be used in the manufacture of adhesives and paper coatings and has been combined with alkyd resins to form hard-bake enamels. With further processing, the resin is used to produce molding compounds.

5-18. Other Ingredients of Urea Molding Powders.—The main appeal of urea plastics is in their color variety. In order to maintain the variety of colors, only general-purpose compounds can

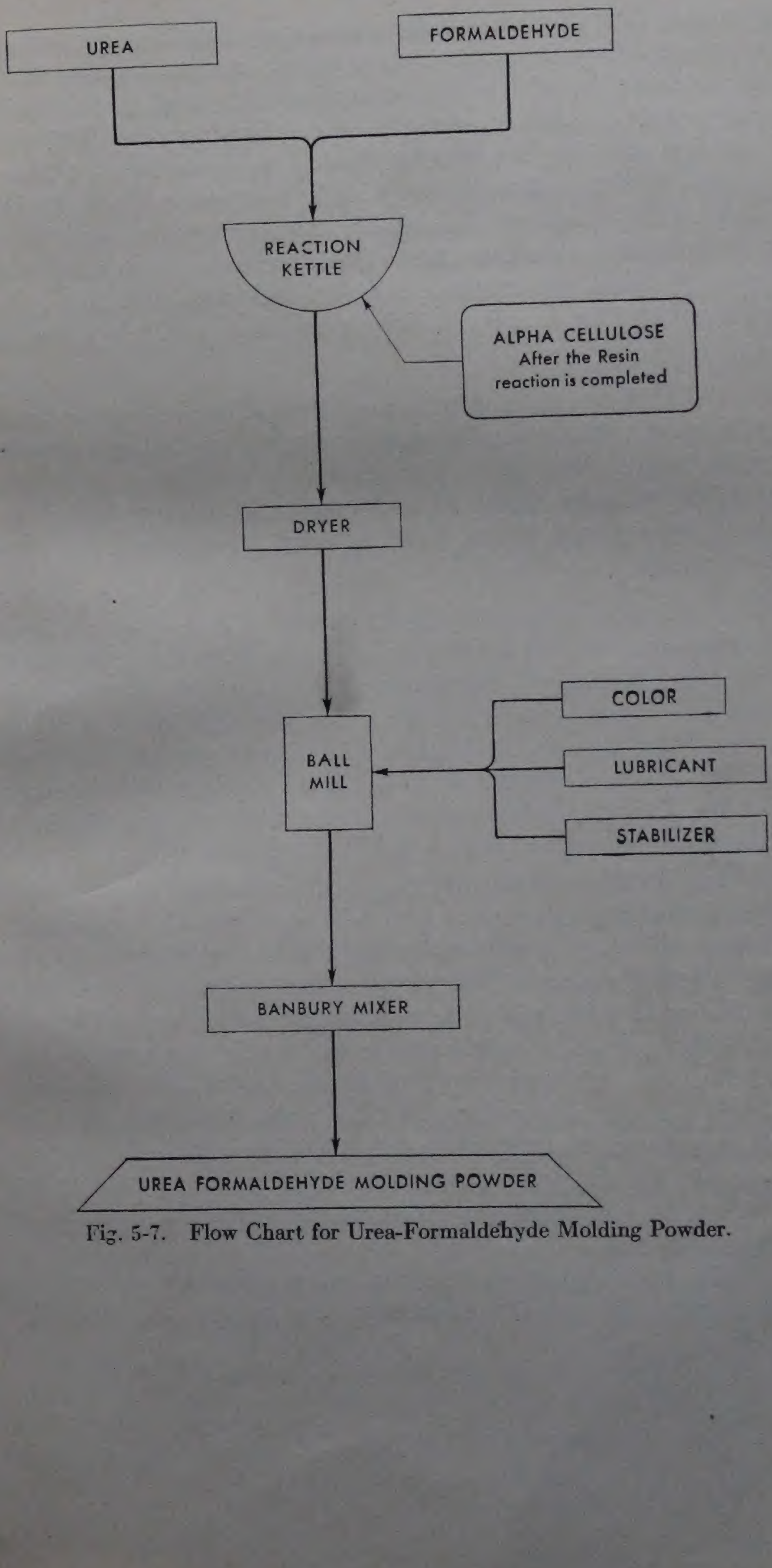


Fig. 5-7. Flow Chart for Urea-Formaldehyde Molding Powder.

be made. The filler universally used for urea molding compounds is pure cellulose. If canvas were the filler, impact strength would be obtained but color would be sacrificed. A small per cent of a fatty acid or calcium stearate is employed as the lubricant. Vegetable oils function well as plasticizers. Since urea is affected by the *p*H of the solution, the dyestuffs incorporated for imparting color must be neutral or acid. The accelerator must also be an acid-producing substance. Zinc chloride or ammonium chloride is generally used. Retarders are never used with urea materials. A flow chart for urea-formaldehyde molding powder is shown in Fig. 5-7.

5-19. Preparation of Cellulose Filler.—Chemically pure wood cellulose, which is generally referred to as alpha-cellulose, is highly refined and is pure white. For convenient handling it is usually supplied in large sheets of blotter-paper thickness, and these sheets are fed to a fuzzing machine which reduces them to a fine, wispy mass.

5-20. Beating and Drying Resin and Filler.—Urea molding powder can be compounded by calender-rolling the resin, filler, and other ingredients together until the desired consistency is obtained. The most widely used method of compounding is known as the Three-B method. The name of the process was derived from the first letter of the names of the three machines used to carry out the compounding operation: beater, ball mill, and Banbury mixer.

In the Three-B process the resin solution is placed in an open beater mixer, which is not to be confused with a kneader. The beater mixer produces a slapping, rather than a kneading or grinding, action. The wispy mass of cellulose is slowly fed to the beater in the cold state, as any heat would begin to polymerize the resin. The resin solution thoroughly impregnates the cellulose and, when the required amount of cellulose has been added, a slushy solution results. The beater is covered, and the solution is vacuum-dried while it is still being beaten. The drying is continued until the slushy solution changes to crumbs, at which stage the vacuum is discontinued and the material is removed from the beater.

The material coming from the beater resembles popcorn, by which name it is usually referred to. The popcorn contains only

two of the six basic ingredients: the binder and the filler. The ball-mill operation involves the remaining four ingredients: color, lubricant, plasticizer, and accelerator.

Although the vacuum-drying operation in the beater removes all the excess water, the popcorn retains internal moisture which must be removed before further processing. This thorough drying operation presents difficulties, as prolonged heating to remove every trace of water would cause hardening of the resin. Further drying can be accomplished by placing the popcorn on trays in a thermostatically controlled oven. By gradually stepping up the heat and at the same time circulating air through the oven, moisture is removed without hardening the resin.

A continuous conveyor set up to run through an equally long oven provides a better means of drying the popcorn than the thermostatically controlled oven. The conveyor belt runs through an oven which is built in sections so that any section can be maintained at any desired temperature. The conveyor carries the popcorn through the oven very slowly. The temperatures of the various sections are graded so that the material is made to lose its moisture very slowly. As the material emerges from the drying chamber, it is immediately placed in sealed containers to prevent the absorption of moisture. The containers are then either stored or taken to the ball mills for further processing.

5-21. **Ball-Milling.**—Ball mills consist of revolving cylinders that contain balls. When the cylinder revolves, the action of the balls is somewhat like the blows of hammers, crushing the material in the cylinder. The tumbling balls generate heat that must be removed to prevent transforming the resin into the C-stage. The heat is removed by means of a brine-filled jacket, and the material remains cool enough to keep the resin from being damaged.

The dried popcorn is put in the ball mill along with coloring matter, lubricant, plasticizer, and accelerator. The accelerator must be of such a nature as not to react chemically with the urea resin in the ball-mill operation. Acid salts, such as ammonium chloride, which decompose on heating to yield acids, are suitable accelerators. The amount of accelerator added depends on how far the resin has progressed in its preparation. When the ball mill has

been charged and set in operation, the popcorn is reduced to a fine powder and the ingredients are thoroughly mixed.

The duration of ball-milling depends on two factors: the surface hardness of the popcorn and the ability of the color to disperse uniformly. The lower the moisture content of the popcorn, the harder the popcorn and the longer the time required to break down the popcorn and mix all the ingredients. High moisture content is undesirable because the popcorn then becomes sticky and good dispersion of the ingredients is impossible. Good dispersion of the coloring matter, of which only a small amount is used, and of the lubricant and plasticizer is required. If the mixture is not homogeneous, the rate of cure and the slipperiness will vary.

If conditions are ideal, several hours are required to achieve uniformity. The material coming from the ball mill is a very fine powder. Check tests for color are sometimes made, but, as a rule, are not necessary. Since no heat is used in the compounding operation, color standards may be set up. This means that definite amounts of resin, color, plasticizer, and lubricant will always yield a mix of the same color. Only when the duration of ball-milling is excessive is there danger of off-shading the color of the mix. The minor ingredients are always checked for color to make sure that they will not impart their own color characteristics to the mix.

5-22. **Banburying.**—Since the powder that comes from the ball mill is too fine for use as a molding powder, except in special cases where consumers have special machinery, it is put through a Banbury mixer, which granulates it. Essentially the mixer consists of an enclosed jacketed chamber which is internally fitted with spiral blades mounted on two cored shafts to form rotors. These shafts are held in place mechanically so as to produce no axial motion. By spacing the shafts close together and revolving them so as to oppose each other, a granulating action is produced on material fed between the blades. The jacketing of the chamber and the coring of the shafts permit the use of steam for heating the material to a desired temperature. The powder from the ball mill is fed to the Banbury mixer through a side hopper. To allow for better flow of material through the mixer, a vertical plunger mounted above the blades is employed. On the down stroke, the

plunger presses material against the blades. The mix is granulated and drops into a catch pan below the blades. On the up stroke, the plunger clears the side hopper and allows more material to fall upon the blades.

The mixing chamber, the cored shafts, and the vertical plunger of the mixer are heated by steam. The plunger forces the material against the rotors, which heat it. When the material has absorbed a little heat, it becomes slightly tacky, forming larger aggregates and eventually granules. The granules, brushing against one another, pass through the spaces between the rotors and gather in the catch pan directly below the rotors.

When the complete charge has been granulated, it is screened. The granules that are too large are agitated on the screen to break them down to the proper size. The particles that are too small to be used as molding granules are put back into the Banbury machine for regranulating. The final screened material that comes from the Banbury mixer is the urea molding compound. As a general rule the screens are set up in series with the mixer so that, once a charge is placed in the machine, granulating and regranulating operations are automatic. The only precaution that must be taken in using a Banbury mixer is to control the addition of heat so as not to affect the state of the resin.

5-23. Flow.—Urea plastic material is used in the making of buttons and reflector globes, as well as other things. The sizes of articles made from urea vary so greatly that it would seem that many formulations (degrees of flow) are necessary to cover every case. Actual molding experience has proved that four degrees of flow are sufficient. The flows are extra soft, soft, medium, and hard; and they are designated by letters. The extra soft and soft flows are used in transfer molding and in the compression molding of long-draw articles, such as radio cabinets and electric-light reflectors. The hard flows are used for small articles that do not require much travel of the molding material. The bulk of applications fall in the medium flow. A medium-flow, white, translucent urea compound was used to make the articles shown in Fig. 5-8.

5-24. Cure.—In urea, as in other thermosetting compounds, there is an inseparable relationship between flow and cure. The softer the compound, the longer the cure; the harder the compound, the shorter the cure. The amount of plasticizer in the

(Courtesy of Libbey-Owens-Ford, Plaskon Division)

Fig. 5-8. Tableware Made From Urea Plastics.

formulation determines the hardness or softness of the compound. Although cure depends primarily on the amount of plasticizer present, it also depends on the state of the resin. The resin stage, as in the case of the phenolics, is called the A-stage. The compounding stage may be called the B-stage, but it must be remembered that the resin itself does not undergo any change. Because the A-stage and the B-stage of the urea resins are exactly the same, it may be said that the ureas go through only two stages. For all practical purposes it is best to think of urea as passing through two chemical stages, but three processing stages.

5-25. Formulation.—The urea resin is the binder of the compound. In general, pure wood or cotton cellulose is used as filler. The black and the brown ureas, however, are filled with wood flour. A small per cent of a fatty acid or calcium stearate is employed as lubricant. Of the plasticizing oils, the vegetable oils function well with the ureas. Urea compounds of crystal clarity have been produced; but, because of the absorption of moisture and the necessity of using an acid accelerator, the crystal clear effect is obscured in a molded article. For this reason, no trans-

parent urea compounds for molding are marketed. Ureas are available in all colors, degrees of translucency, and opacities. Since pH is important, best results are obtained when the coloring materials are acid or mordant dyes or inorganic pigments. Retarders are never used with urea materials; however, an excess of lubricant will act as a retarder. Zinc chloride and ammonium chloride, which are acid-producing substances, are used as accelerators. A typical formula for a molding compound is as follows:

	Per Cent
Binder (urea resin)	40
Filler (alpha cellulose)	57
Lubricant (calcium stearate)	¼
Color (titanium dioxide)	1¾
Accelerator (zinc chloride)	1

Great care must be taken in the storage and handling of urea molding material. When exposed to temperatures above 80° F, this material becomes hard, since the acid liberated by the accelerator begins to set the resin. The storage temperature should be approximately 70° F. Since urea compounds pick up moisture rapidly, they should be kept sealed until ready for use.

5-26. Applications.—Urea molding powders, fine or granular, are molded in the same type of mold used for phenolics, but the pressures used are greater than those used for phenolics. The molded articles are resilient and have exceptional strength. Moreover, they are resistant to oils and greases, and have good electrical insulating properties. Buttons, stove knobs and handles, bottle closures, clock and radio housings, tableware, and containers are made of urea. Translucent urea resin is replacing opal glass in the electric-lighting field, largely for its excellent light transmission and diffusive qualities. All kinds of shades and reflectors are manufactured for use in homes, railway cars, and automobiles.

Water-soluble urea resins are used for laminating paper and cloth, for impregnating textiles for crease-proofness and increased strength, and as heat-setting and cold-setting glues and adhesives. Plywoods bonded with urea adhesives are permanent, strong, and fungus- and bacteria-resistant. Intermediate condensation forms of urea resins applied as coatings and baked have been used as refrigerator enamels. Bakelite Urea, Beetle, and Plaskon are trade names of products made of urea resins.

Thiourea Compounds

5-27. While urea materials have found great favor in the United States, thiourea is prominent in the plastics field in Europe, particularly England. The structure of thiourea is similar to that of urea, an atom of oxygen being replaced by an atom of sulfur. A molecular rearrangement occurs on heating ammonium thiocyanate, resulting in the formation of thiourea, as follows:

$$NH_4CNS \longrightarrow NH_2{-}C{-}NH_2 \quad (S \text{ double-bonded to } C)$$

thiourea

Condensed with formaldehyde, thiourea undergoes the same processes as urea to form resins. Where heat is involved in the production of urea compounds, slightly higher temperatures are necessary to produce satisfactory thiourea products. The compounding with filler and other ingredients is the same as for urea. The thioureas are said to have better moisture resistance than the ureas, although the molding characteristics are not so good.

Melamine

5-28. Structure of Melamine.—Melamine compounds are thermosetting, and belong to the synthetic-resin group. Melamine is a heterocyclic chemical compound that is also called 2,4,6-triamino-1,3,5-triazine; cyanuric acid amide; and cyanuric triamide. Its structural formula, which is shown in Fig. 5-9, indicates that it is basically three molecules of hydrocyanic acid, the acid radical of which has been replaced by an amino group, NH_2. The broken lines separate the three molecules.

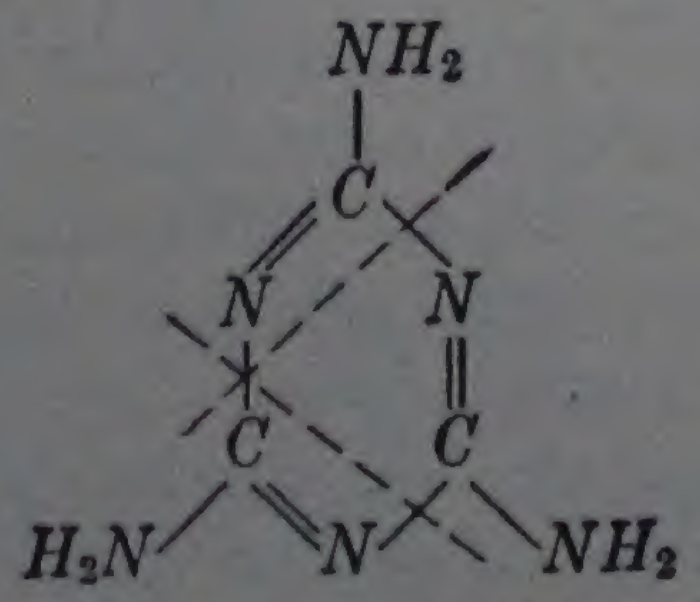


Fig. 5-9. Structure of Melamine.

Of the resinous products which melamine can form by reacting with other compounds, the resins formed by condensing melamine with formaldehyde are of considerable importance. Melamine, when pure, is a crystalline solid that is soluble in hot water, slightly soluble in hot alcohol, and insoluble in ether.

5-29. Resinification.—The condensation of melamine with formaldehyde is a chemical complexity. However, research has shown that long-chain molecules can form by either of two methods; that is, molecules of a resin chain can be connected by a methylene linkage or by an ether linkage. Some similarity exists between the reaction mechanism of the ureas and the melamines. A product known as a methylol compound is first produced upon reacting melamine with formaldehyde. Linking a large number of the methylol compounds results in a resinous product, as represented by the equation in Fig. 5-10.

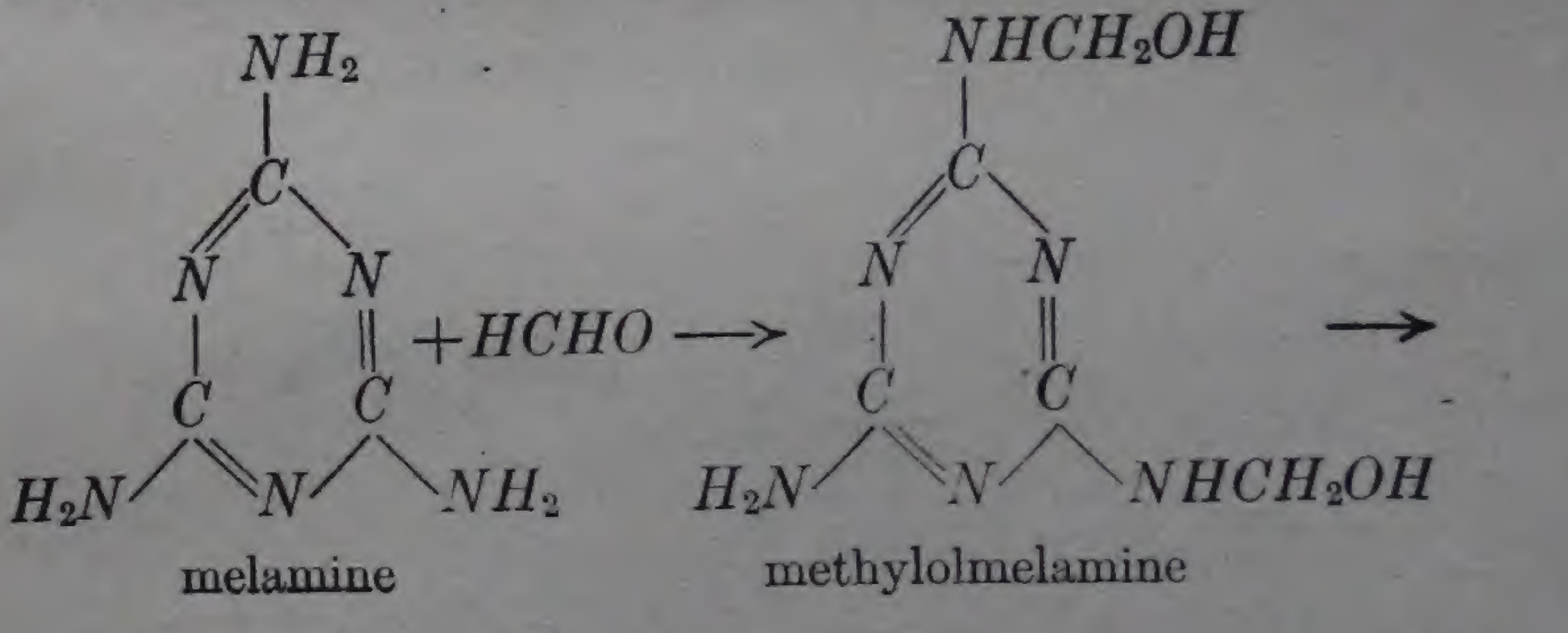


Fig. 5-10. Condensation of Melamine With Formaldehyde.

5-30. Melamine Synthesis.—Commercially, melamine is prepared from such materials as limestone, coal, and air. A mixture of coke and limestone is heated in a furnace by means of an electric arc to a temperature of 2000° C or higher. The product formed,

calcium carbide, will react with nitrogen, derived from air, to yield calcium cyanamide. Many organic chemicals are derived from cyanamide, but the one most important to melamine is dicyanodiamide made from calcium cyanamide and water. Reactions typical of those just mentioned are as follows:

$$5C+2CaO \longrightarrow 2CaC_2+CO_2$$

$$CaC_2+N_2 \longrightarrow CaCN_2+C$$

$$2CaCN_2+4H_2O \longrightarrow \underset{\text{dicyanodiamide}}{\begin{matrix} NH_2 \\ \diagup \\ C{=}NH \\ \diagdown \\ NH{-}C{\equiv}N \end{matrix}} +2Ca(OH)_2$$

Melamine is produced by the cyclization of dicyanodiamide in the presence of anhydrous ammonia, under a pressure of from 150 to 1,500 pounds per square inch and at a temperature between 100° and 400° C. This process is represented in Fig. 5-11. Other

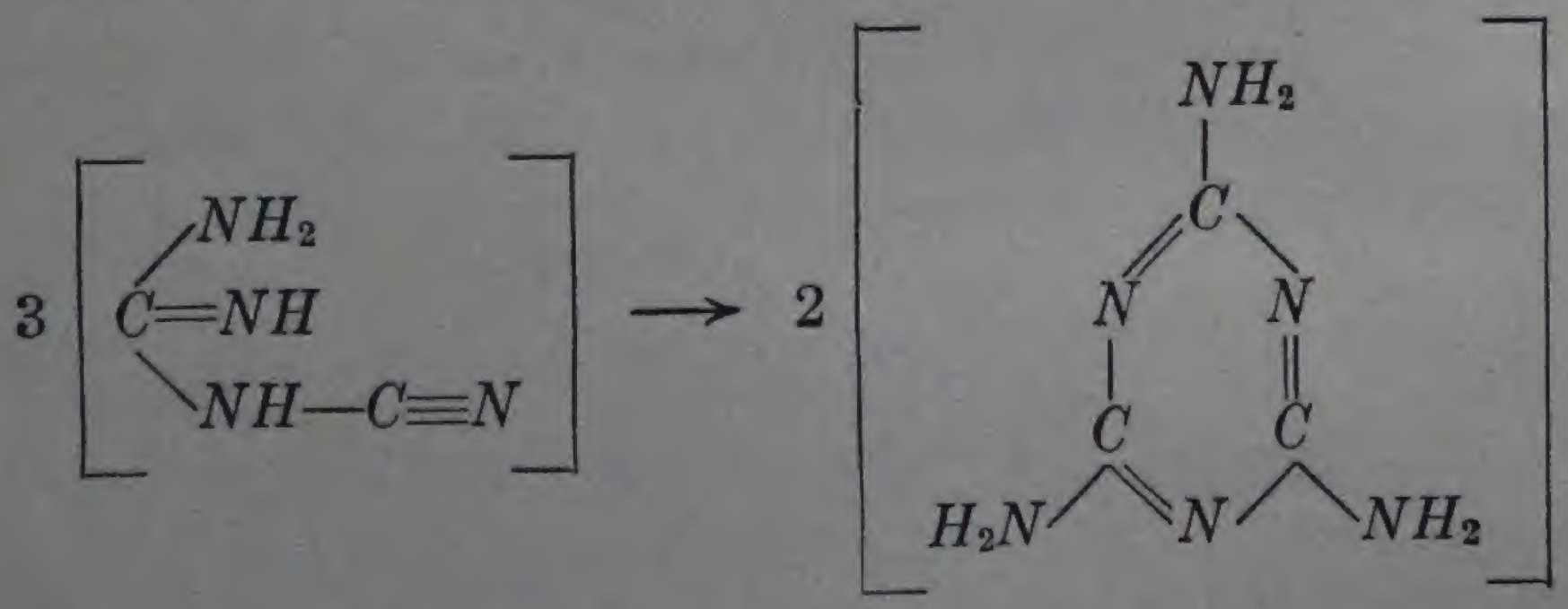


Fig. 5-11. Cyclization of Dicyanodiamide.

methods used to obtain melamine include the action of titanium chloride on hexamethylene tetramine, and extraction from melam, a natural substance.

5-31. Ingredients of Melamine Plastics.—All sorts of fillers can be incorporated in melamine compounds. When alpha-cellulose is compounded with melamine, a composition very similar to the ureas is obtained. The properties of melamine resin are an improvement over those of the urea resins, so that better properties in the molded articles can be expected. Melamine resins are more expensive than the urea resins. The melamine compounds are produced in quantities mainly for superior properties of resistance to electric current and heat. In order to obtain these properties, a filler other

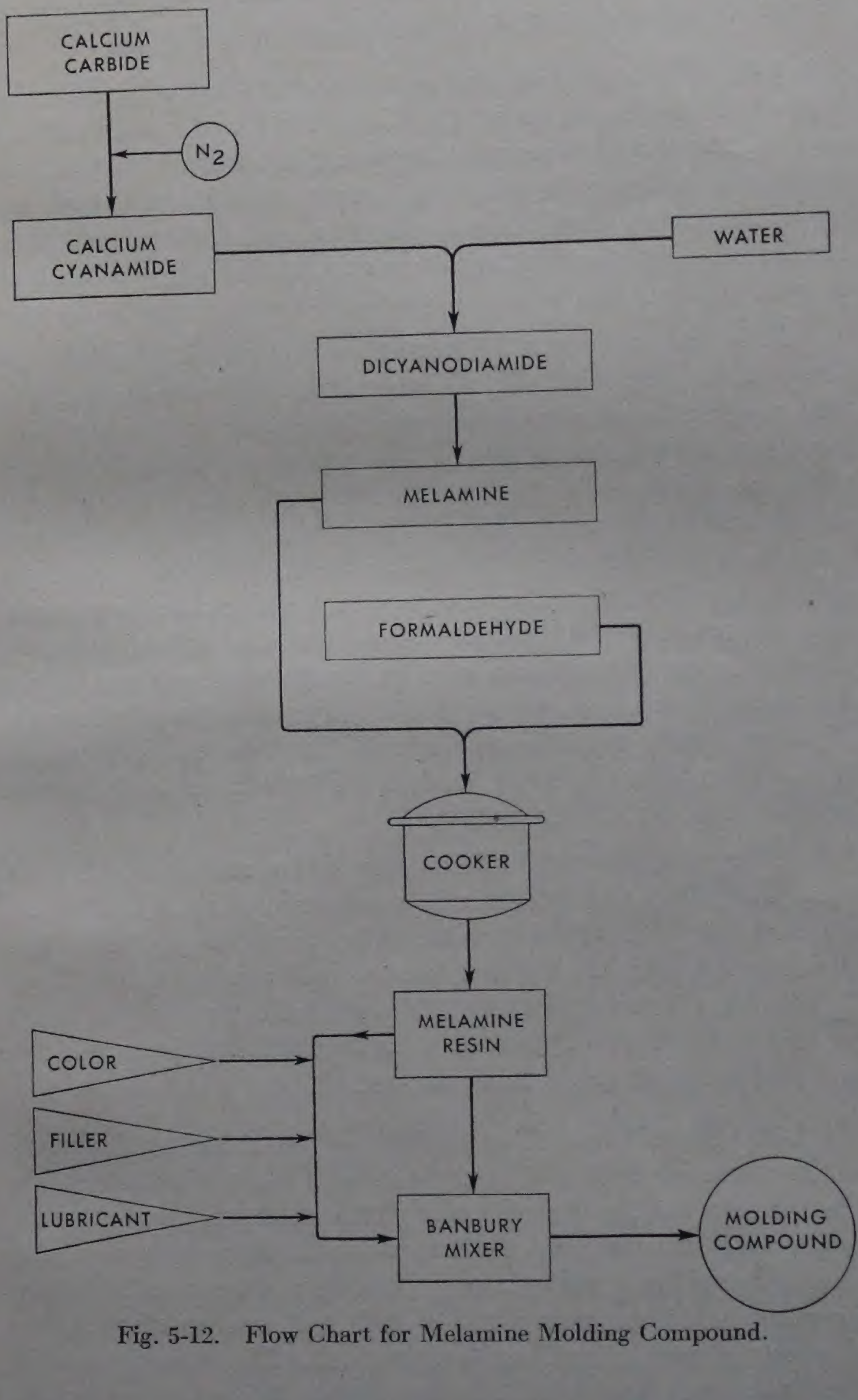


Fig. 5-12. Flow Chart for Melamine Molding Compound.

than cellulose is used. Most of the melamine compounds on the market contain asbestos or spun glass as the filler.

5-32. Molding Compound.—A flow chart for melamine molding compound is shown in Fig. 5-12. Melamine reacts with an aldehyde to form a thermosetting resin. The resin is formed in a cooker by bringing together the proper amounts of ingredients under the proper conditions of *p*H, time, and temperature. These conditions depend on the use to which the finished product is to be put.

Melamine resin can be converted into molding powder by the conventional methods of hot calendering and Banburying. The powdered resin is premixed with filler, color, and an accelerating agent. If the molding powder is to be used for electrical applications, no lubricant is used, since it would impair the electrical characteristics of the compound. The manufacture of the molding compound is the B-stage. The A-stage melamine resin is sparingly soluble in water, being like the phenolics and unlike the ureas in this respect. All the precautions of phenolic rolling must be observed with the melamines. The hardness or softness of the compound depends on the degree of polymerization of the resin. Melamine resins are infinitely more difficult to handle than the phenolics in that the set is harder. This condition tends toward brittleness in the molded articles.

If the material is calendered, the sheets must be broken up into small pieces and fed through a pulverizer; but, if a Banbury mixer is used, the screened material is the molding powder. The melamine powders are blended to insure uniformity of flow. Even though the melamine resins are not very soluble in water, the molding compounds are so hygroscopic that the material is always kept in sealed containers until ready for use.

5-33. Use of Cotton Rag as Filler.—One of the developments in the melamine field has been the incorporation of cotton rag as filler. Exceptionally high flexural strengths have been obtained by the use of this material. Cotton-rag materials are not, as a rule, manufactured by a rolling process, because rolling would destroy the strength of the weave in the cloth and impregnation of the filler would not be uniform or thorough. The resin is usually applied by spraying or tank impregnation. Before the compound

is ready for use, all the excess solvents must be evaporated. A controlled drying oven is satisfactory for this purpose.

5-34. **General Remarks.**—Melamine is capable of reacting with alcohols, with simple sugars, such as glucose, and with phenol. The condensation products produced with formaldehyde, however, are by far the most important. For melamine-formaldehyde resins to be of use as lacquers and varnishes, they must be compatible with the ingredients commonly used in paints and varnishes. This compatibility is usually obtained by condensing melamine and formaldehyde in the presence of an alcoholic medium, the condensation products being extremely tough, water-white, and heat-resistant films. Solutions of the resin in organic solvents are used as impregnates for paper, canvas, asbestos, and glass cloth. When melamine resins are mixed with alkyd resins, superior protective coatings are obtained. More recently, a melamine hot-set adhesive has been marketed for plywood bonding.

5-35. **Formulation.**—With alpha-cellulose as filler, the melamines can be produced in all colors from a light translucent white to an opaque black. The formulations for compounds of this kind are similar to the urea formulas. When a mineral filler is used, the colors are limited to opaques of the darker shades.

A typical formula for a material that offers high resistance to electric current and heat would be as follows:

	Per Cent
Binder (melamine resin)	44
Filler (asbestos)	54
Color (inert pigment)	1
Accelerator (alkaline curing agent)	1

No lubricant or plasticizing agents are used, since they would impart lower values to the physical, mechanical, and electrical properties of the compound.

5-36. **Applications.**—Notable properties of the melamine plastics include exceptional resistance to electric current, high dielectric strength, and resistance to heat. These factors make melamine molding powders especially suitable to the molding of electrical terminal blocks, distributor heads, and circuit breakers. Compression and transfer molding are the best methods of handling

melamine molding powders. Tableware and buttons are other articles that demonstrate the superior resistance of melamines to hot water, food staining, and shock. Resins for plywood bonding, impregnating, and coating solutions appear on the market under such trade names as Melmac and Plaskon Melamine.

Lignin

5-37. Chemistry of Lignin.—Lignin resins by themselves are thermoplastic. Lignin plastics, however, are classified as thermosetting of the combined natural and synthetic resin type. Wood contains from 25 to 30 per cent of lignin. Although the exact structure of lignin is not fully understood, it is believed to be composed of chains of polyhydroxy phenols. Lignin is the bonding agent for the cellulosic fibers in wood; so it is a natural resin.

5-38. Sources of Lignin.—Since lignin resin is found in wood, all the forests are the natural source of supply. Although this is true, no tree was ever cut down solely for the purpose of obtaining lignin resin. Waste wood, in the form of sawdust and wood shavings, is the ideal source of supply. Also, the acid sulfite process for making paper is an abundant source of lignin. From it a great deal of sulfite liquor was wasted as sewage. Utilization of this waste liquor has held the attention of chemists for years. Recent developments have proved that the sulfite liquor contains a high percentage of lignin. The lignin is in solution and in a sulfonated form.

5-39. Lignin-Enriched Products.—Lignin is used in two forms by the compounder: as a resin and as a lignin-enriched filler. The lignin-enriched filler is prepared from waste wood chips and sulfite liquor. The waste wood contains a small amount of lignin, and the sulfite liquor enriches the product with its own lignin content. The process is as follows: The wood chips and waste liquor are placed in a digester together. Under pressure the wood hydrolyzes and softens considerably. The natural lignin along with the waste-liquor lignin is thoroughly distributed throughout the wood fibers. The lignin-enriched wood is removed from the digester and is thoroughly washed to remove all soluble matter and any excess alkali. The chips have the same appearance as before the treatment, except that the color has changed to a dark brown. The

chips are put through a grinding operation to be reduced to filler size for molding compounds.

5-40. Resinous Products.—Lignin resin is formed from waste sulfite liquor. The sulfite liquor is given an acid treatment to precipitate the resin. A water wash is used to free the precipitate from impurities and any excess acid. Then the resin is filtered by suction and is allowed to dry in cakes, which are broken up in a chopper and fed through a pulverizer.

The lignin-resin powder is used mainly for extending other resins, phenol-formaldehyde resins being particularly suited for extension with lignin. An ordinary general-purpose phenolic, which contains from 40 to 50 per cent of phenolic resin, can be modified by the addition of lignin-resin powder. The best results have been obtained from a mechanical mixing of lignin-resin powder with phenol-formaldehyde resin.

5-41. Phenolics Extended With Lignin.—In order to effect complete mixing, the lignin and phenolic resins are mixed in the liquid suspension form. The phenolic resin is suspended in water while the lignin resin is dissolved in alcohol. The phenolic-suspension solution is slowly added to the lignin solution with vigorous stirring. The lignin soon completely dissolves in the phenolic suspension. The phenolic content in a molding powder can be cut as much as 50 per cent, without affecting the physical or chemical properties of the molded articles, if the amount of phenolic resin removed from the formula is replaced by lignin resin. This represents quite a saving, since lignin resin, being made from waste materials, is much cheaper than synthetic phenolic resin.

The method applied in the compounding stage, or B-stage, of an extended phenolic is different from that for the straight phenolics, but the principle is the same. In this instance, a liquid rather than a powder is used. The liquid state insures more uniform impregnation of filler for the following reason: There is a distinct difference between the melting point of the lignin resin powder and that of the phenolic resin. If a mix of the two were calendered, one would soften before the other and a non-homogeneous compound would result. Liquid resin, color, and lubricant are mixed with the filler in a Koller-gang, or "putty chaser," type of mixer. In this way, the liquid resin thoroughly permeates the filler. This premixing is equivalent to the spiral-blade mixing of the straight

phenolics. The continuous rolling of the stone generates quite a bit of heat; and in most cases a calender rolling is not necessary, as the heat generated is sufficient to advance the mixture to the molding stage, or C-stage. The compound coming from the putty chaser is granular. Any fines are removed by screening, and the resultant compound is the lignin-extended phenolic molding compound. Extended compounds have been confined to blacks and dark browns.

5-42. Lignin-Enriched Filler.—Lignin-enriched filler is used in the manufacture of molding compounds as a replacement for wood flour. Owing to the fact that the filler has a high lignin content, less phenolic resin may be used in formulating with this filler. The prepared filler is mixed with resin, lubricant, accelerator, and coloring matter in a spiral-blade mixer. After a short mixing period, the material is calendered the same as if it were a straight phenolic compound. With lignin-enriched material used as the filler, molding compounds of the phenolic type have been made with as little as 25 per cent of phenolic resin.

5-43. Lignin Laminates.—Lignin compounds, thus far, have made the greatest inroads on the laminated field. For laminated applications, lignin-enriched wood is thoroughly defibrated into a fuzz, which is thoroughly washed to remove all extraneous matter. This process is similar to the fuzzing of alpha-cellulose in the urea process. The fuzz is placed in a paper-beating machine, and to it is added a plasticizer. Upon beating of the mixture, a thick pulp results, which can be fed to a regular paper-making machine. Thin sheets of lignin paper are formed in the machine. The steps in this process are actually the same as those for making paper, except for the addition of the plasticizer. The sheets of paper are stacked one upon the other in a laminating press, the number in a stack depending on the thickness to be obtained in the laminated board. Upon pressing and thorough curing, a laminated board results.

Some experimental work has been done with lignin-enriched filler as a pulp molding compound. The lignin-enriched pulp is suspended in water in a beater. The suspended solution is then poured into crude shapes and is felted or preformed by screen suction. The crude article is dried and then subjected to a regular molding procedure, similar to the procedure for asbestos-pulp molding material.

5-44. Commercial Possibilities.—All the commercial lignin products to date have used phenolic resins as the main binder. Investigation is under way as to the possibility of use with urea and some of the cellulose-derivative compounds. There is no reason why compounds such as urea-lignin should not be entirely satisfactory. It should only be a short time before lignin is in commercial use in many plastic materials.

The major advantage of lignin is its low cost, which enables lignin phenolics to be manufactured at a cost approximately 20 per cent less than that of straight phenolics. The other main advantage of lignin is its unlimited supply. The production of synthetic resins depends on basic chemicals, which are difficult to obtain in wartime. Lignin is able to stretch whatever supply is available. For instance, 50 pounds of straight phenolic resin will produce roughly 100 pounds of molding compound. If lignin is incorporated to the extent of 50 per cent of the phenolic content, the same 50 pounds of phenolic resin will make almost 200 pounds of compound, and at a lower cost.

5-45. Formulation.—In general, the ingredients used for lignin resin and lignin-enriched molding compounds are the same as for the straight phenolic compounds. The amounts of the various ingredients will depend directly on how much substitution of lignin for phenolic has been made and on the chemical and physical properties desired in the finished compound. Naturally, a composition containing 25 per cent of lignin and 25 per cent of phenolic resin will have values for the various properties different from a compound containing 15 per cent of lignin and 35 per cent of phenolic resin. Replacing up to 50 per cent of the phenolic resin will yield satisfactory molding compounds for ordinary purposes.

A typical lignin-resin formula is as follows:

	Per Cent
Binder	
(lignin resin)	18
(phenolic resin)	22
Filler (wood flour)	56
Color (carbon black)	2.5
Lubricant (calcium stearate)	.5
Accelerator (lime)	1

A typical formula for a lignin-enriched product is as follows:

	Per Cent
Binder (phenolic resin)	25
Filler (lignin-enriched filler)	72
Color (carbon black)	2
Lubricant (calcium stearate)	.5
Accelerator (lime)	.5

5-46. Applications.—The diversified uses for lignin laminates include electrical switchboards, spool-heads, insulating washers and spacers, name-plates, door-kick and push plates, cabinets, and foundry patterns. Lignin laminates are resistant to electric current and have good strength as evidenced by their usage in the electrical industry. Low moisture absorption and durability account for their other applications.

Lignin-phenolic molding compositions are used for buttons, closures, decorative novelties, and games. Their usefulness in these fields is due to excellent shock resistance and impact strength. Conditions for the molding of straight phenolics need not be altered materially for the mixed composition. Lignolite, Benalite, Lignin, Textolite, Lignin Laminated, and Benaloid are trade names of lignin products.

Chapter Six

Thermoplastic Resins

Cellulose Acetate

6-1. Acetylation of Cellulose.—Cellulose acetate is classified as a thermoplastic of the cellulose derivative type. The chemistry of cellulose acetate is similar to that of cellulose nitrate. Instead of nitration, the cellulose undergoes acetylation, which is the replacing of the hydroxyl groups by acetate, or acetyl, radicals.

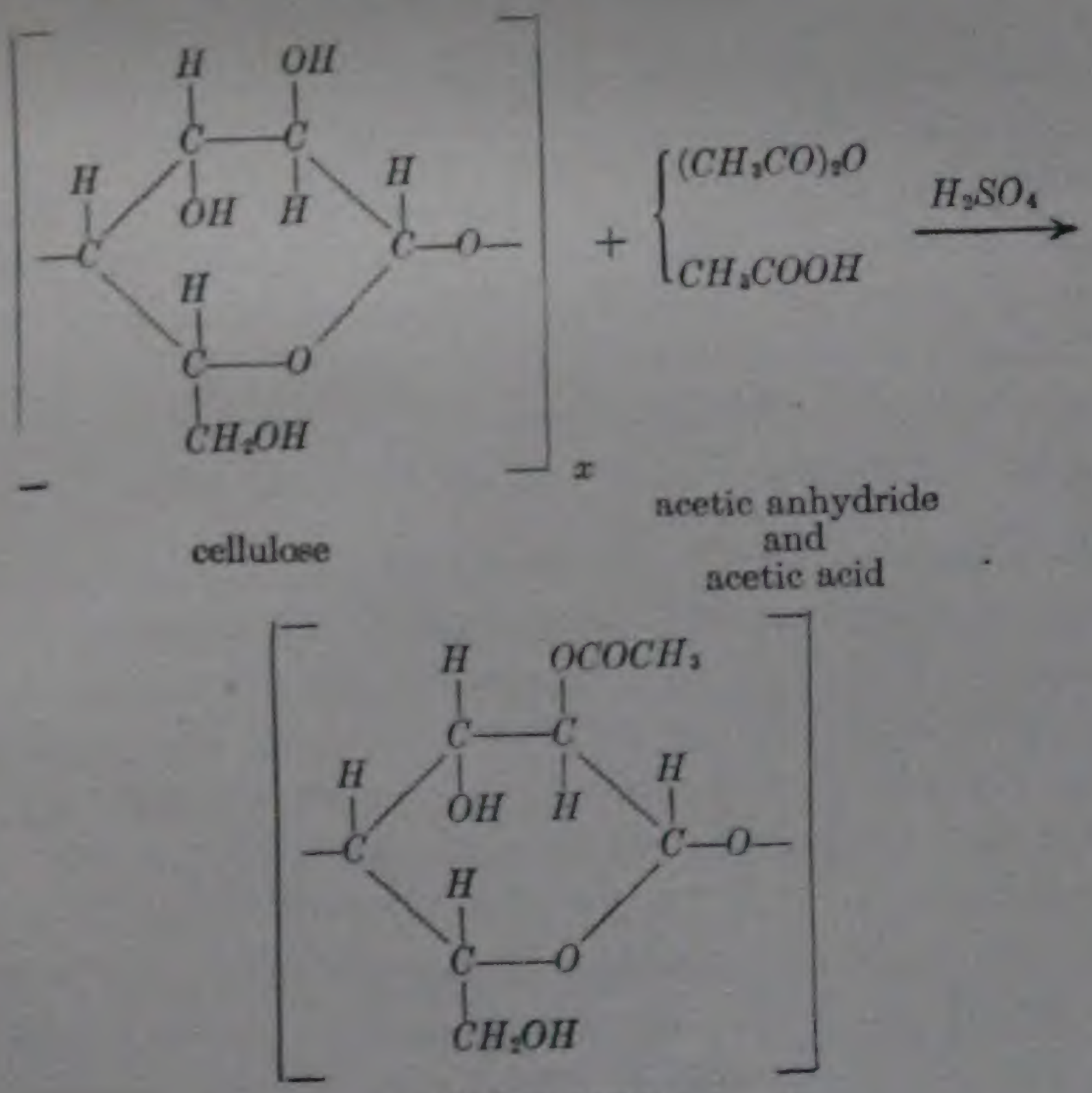


Fig. 6-1. Reaction for Production of Cellulose Acetate.

6-2. Acetyl Content.—The reaction between cellulose and a mixture of acetic acid and acetic anhydride, in which sulfuric acid is used as the catalyst, produces commercial cellulose acetate according to the reaction shown in Fig. 6-1.

The acetylation of cellulose encounters situations similar in many respects to the nitration of cellulose. There are a great number of hydroxyl groups where the reaction can take place. The replacement of hydrogen by the acetyl radical is haphazard. Complete acetylation is never attained. Cellulose acetate used for molding powder has an acetyl content of from 52 to 61 per cent. Acetate used for making rayon has an acetyl content of from 50 to 54 per cent. The higher the degree of acetylation, the less soluble the material becomes. There are many cellulose acetates that could be manufactured. In general practice, there are three commercial acetates, having low, medium, and high acetyl contents, respectively. The acetyl contents for the three grades are: low, 52 to 54 per cent; medium, 54 to 56 per cent; high, 56 to 58 per cent.

6-3. Sources of Cellulose and Acetic Acid.—The cellulose used in the manufacture of cellulose acetate is the same as that used for the nitrate. The sources of supply, therefore, are the same. The acetic acid used is obtained mainly from acetylene gas. Since ordinary vinegar is a dilute, impure form of acetic acid, the concentrated acid can be obtained by repeated distillation of vinegar. Some acetic acid is obtained from the destructive distillation of wood. Acetic anhydride is prepared from acetic acid.

6-4. Plasticizers.—Cellulose acetate may be molded without the addition of a plasticizer. The unplasticized material possesses an extremely high working temperature. At very high temperatures, decomposition of the cellulose is evident. The physical and chemical properties of unplasticized acetates are not very good. They are brittle and the mechanical strengths are low. Unlike cellulose nitrate, there is no one plasticizer that is suitable for all applications of cellulose acetate. In the phenolics, the properties usually depend on the kind and amount of filler used. In cellulose acetate, the properties depend mainly on the kind and amount of plasticizer used.

In connection with cellulose acetate, plasticizers are thought of as high-boiling-point liquids that act as solvents for the acetate. In acting as solvents, they gel the acetate flake, and this action is accompanied by a lowering of the melting point. Various plasticizers are used for obtaining different effects in the molding compound. Just as there is no one plastic that is suitable for all pur-

poses, there is no one plasticizer that is satisfactory to produce all the desired properties in a molding compound. Table 6-1 lists some of the more common plasticizers with their functions. Most of the plasticizers in use today are synthetically made.

TABLE 6-1

PLASTICIZERS AND THEIR FUNCTIONS

Plasticizer	Main Function
Dimethyl phthalate	Water resistance
Diethyl phthalate	Softening
Tributyl phosphate	Toughening
Triphenyl phosphate	Flame proofing and hardening
Methyl phthalyl ethyl glycollate	Softening and toughening
Ethyl acetanilid	Hardening

6-5. Dyestuffs.—One of the outstanding properties of cellulose acetate is its ability to match all colors of the spectrum. Not all dyestuffs can be used. It is best to use only those dyestuffs that are entirely compatible with the acetate. Since dyestuffs are added in a solvent solution, it is also necessary to have that agent compatible with the acetate. The dyes most frequently used are oil-soluble and spirit-soluble dyes. In order to produce truly opaque plastics, pigments and insoluble dyes or lake toners can be used. Since opaque plastics will not permit transmission of light, dispersion does not have to be perfect. The rolling operation will take care of the uniformity of color.

6-6. Preparation of Acetate Flake.—The steps in the production of the various types of cellulose-acetate plastics are shown in the flow chart in Fig. 6-2. Two general processes for the manufacture of cellulose acetate are the solvent process and the non-solvent process. The preparation of the cellulose-acetate flake is the same in both methods. The purified cotton linters are placed in a large monel-, chrome-, or nickel-lined kettle. A mixture of acetic acid and acetic anhydride is added. After several minutes of thorough agitation, the sulfuric-acid catalyst is added. The proportions of the mix in conjuction with the acetylating conditions

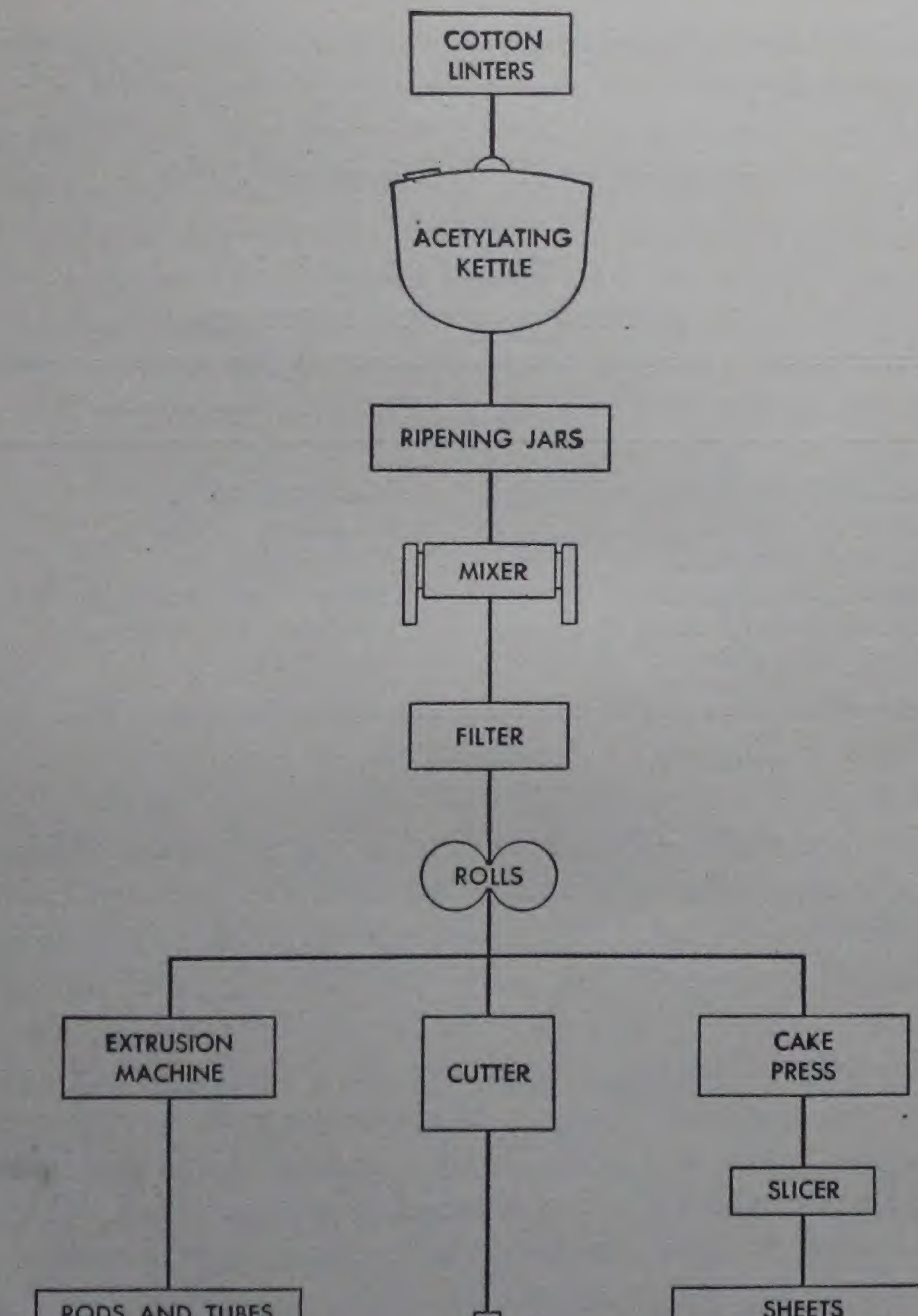


Fig. 6-2. Flow Chart for Production of Cellulose-Acetate Plastics.

(*Courtesy of the Tennessee Eastman Corp.*)

Fig. 6-3. Thick Syrup From Reaction Kettle Being Poured Into Storage or Ripening Jars in Production of Cellulose Acetate.

determine the type of cellulose acetate which will be formed. An intermediate formula would be as follows:

	Per Cent
Cotton linters	12
Acetic anhydride	39
Acetic acid	44
Sulfuric acid	5

The mixture is held below 70° F for a period of about 5 hours, during which the mix is constantly agitated. In being acetylated

the cotton linters lose their fibrous appearance, and a thick syrupy liquid, as shown in Fig. 6-3, is produced. The syrup is poured from the kettle into large storage vats. About 5 per cent of water is added to dilute the excess acids and to prevent further reaction. The water acts as a hydrolyzing agent. This procedure is called ripening. As hydrolysis proceeds, the cellulose acetate is precipitated.

6-7. Ripening and Precipitation.—The ripening process requires about 5 days. The temperature is always held below 90° F. It is possible to precipitate the flake all at once by adding a large volume of water to the syrup in the acetylating kettle. Experience, however, has proved that acetate precipitated in this manner does not possess the strength that slowly precipitated acetate possesses. Bulk precipitation is also more difficult to handle. If a large volume of water is added to a cellulose-base lacquer, the cellulose precipitates instantaneously in a gummy mass. If water is added a drop at a time, flake precipitation results. The same is true of plastic-acetate precipitation.

At the end of the 5-day period, when the acetate has ripened enough for complete precipitation, the storage tank is emptied into a tank of cold water. The cellulose acetate, which immediately precipitates as flake, is washed thoroughly to remove completely all traces of acid. The material is then dried in a centrifuge to remove all adhering water. The acid present when the flake is precipitated and in the wash water should be recovered for reuse.

6-8. Solvent Process.—The solvent process for the manufacture of acetate molding compound involves the dissolving of the flake. The type of flake that has been manufactured will determine the selection of solvents; for, the higher the acetyl content of the flake, the greater the difficulty encountered in dissolving it. As a general rule, it may be said that the higher the acetyl content of the flake, the lower the carbon-chain content of the solvent. As this solvent must be evaporated later on, its boiling point must be low. Acetone is the most widely used solvent.

The flake is placed in a kneading machine, and enough acetone is added to make a doughy mass, as illustrated in Fig. 6-4. Mixing is continued until the material is uniform. The plasticizer is then added and is thoroughly kneaded into the mix.

(*Courtesy of Celanese Plastics Corp.*)

Fig. 6-4. Mixing of Cellulose Acetate With Plasticizer in Kneading Machine.

The plastic mass is removed from the mixer and is placed on calender rolls, which are the same as those used in the production of phenolic molding compounds. The dyestuff, previously dispersed in alcohol or some other suitable solvent, is poured onto the mass as it is being calendered. By manipulation of a hand knife, as illustrated in Fig. 6-5, the color is evenly dispersed throughout the mix. When thoroughly homogeneous, the plastic is cut away from the rolls in chunks. In some cases, it is more advantageous to use a mechanical knife and cut the plastic away from the rolls in sheet form.

Since cellulose acetate is permanently thermoplastic, the rolling operation is relatively simple. Both front and back rolls are

Fig. 6-5. Calender Rolls and Hand Knife Used in Processing of Cellulose Acetate. (*Courtesy of Celanese Plastics Corp.*)

heated, the latter being maintained at approximately 300° F while the former is held at about 200° F. Various manufacturers maintain different rolling conditions. The length of rolling time depends on the attainment of complete homogeneity of flake, plasticizer, and dyestuff. As soon as this condition is reached, the material is removed from the rolls. While the process appears to be simple, there is one factor that must be watched rigidly. Plasticizer is added to lower the softening point of the compound. If the temperatures are too high or the rolling operation is too long, some of the plasticizer will volatilize and escape. This will have the effect of raising the softening point of the finished compound. If the dyestuff does not disperse readily, it is necessary to roll longer until thorough dispersion is accomplished. If the dyestuff is not particularly stable toward heat, the additional rolling may have the effect of destroying the color.

6-9. Non-Solvent Process.—The use of a Banbury mixer differentiates the non-solvent process from the solvent process. A mixture of cellulose-acetate flakes and plasticizer is fed to the Banbury mixer through the side hopper. As the mixture is caught between the blades of the rotors, it undergoes a kneading and granulating treatment. The result is a lumpy form of plastic material, as contrasted to the rough sheets coming from the calender rolls. The use of the vertical plunger improves the flow of the material through the mixer. This type of mixer is built with automatic controls so that it can operate continuously, once the hopper has been filled with the plastic mixture.

6-10. Preparation of Molding Compound.—In order to produce a molding compound, the cellulose acetate is put through another step. The material from the rolling or kneading operation must be reduced to a granular consistency. For this purpose, a rotary cutter is used. The cutter consists of a large steel drum, which is free to revolve and is encased by a chamber. Mounted on the drum are several hardened-steel cutting blades. At several points on the inside wall of the chamber are installed stationary cutting blades. There is a clearance of about $\frac{1}{4}$ inch between the rotating blades and the stationary blades. A screened opening beneath the rotary blades allows material of the desired size to pass. The size of the opening is usually $\frac{1}{4}$ or $\frac{5}{16}$ inch.

The cellulose acetate, in the form of cut-up sheets or small chunks, is fed to the rotary cutter through a hopper. The blades that rotate at high speed use the material as a wedge against the fixed blades. Since the force exerted by the blades is greater than the strength of the material, the cellulose acetate is sheared into smaller pieces. The original material is broken up and passes out of the rotary cutter when the particle size is slightly less than that of the screen openings. At this point, the small granules drop into a catch trough. Rotary cutters are made in several sizes, the capacities ranging from 10 pounds per hour for the smallest unit to 1,000 pounds per hour for the largest unit. The granules leaving the rotary cutter are particles of the cellulose-acetate molding compound which is used in the molding press.

6-11. Preparation of Other Forms of Cellulose Acetate.—Cellulose acetate is also fabricated into sheets, rods, and tubes. To manufacture the rod and tube forms, it is necessary to put the granules through a continuous-extrusion machine. Manufacturers sometimes place a small wire screen at the extruding end of the machine, so that the small square bars are diced after they pass through the openings in the screen. The diced particles are called pellets. This method insures uniform granulation to the consumer. The process for making rods and tubes is the same as that described for cellulose nitrate.

There are two processes used for sheet production; the process used depends entirely on the thickness of the sheets desired. Small area sheets with a thickness of from $\frac{1}{4}$ to 1 inch are made by extrusion, the process being the same as that used for rods and tubes. Thin sheets, such as those used for packaging, are sliced from large cakes. The cakes are made by the same process as described for nitrate. All sheet stock must be seasoned.

6-12. Classification of Cellulose-Acetate Plastics.—Because of the varieties of plasticizers and types of flake available, there are many different formulas that can be compounded for cellulose-acetate plastics. Material manufacturers realized this and decided on a general standardization of acetate materials. Complete classification has not yet been accomplished, but enough has been done to permit a survey. The general breakdown is similar to that of the phenolics, although the categories are different. Acetates are classified into seven major types, according to physical properties.

Table 6-2 lists the types of molding compounds with their specific uses.

TABLE 6-2
ACETATE TYPES AND THEIR USES

Type of Acetate Molding Compound	Use
Compression—regular	All around use.
Injection—general	General purpose.
Injection—physical	Rigid surface, good warp resistance.
Injection—mechanical	Good strength in thin sections, such as combs.
Injection—welding	Strong welds after flowing around core pin or inserts.
Injection—special	Tailor made for any special duty application within limitations of the material.
Injection—high acetyl	Good heat and moisture resistance; high degree of form stability.

6-13. Types of Flow.—Flow is defined as the distance a plastic will move through an orifice under specified conditions of time, pressure, and temperature. Each formula is produced in a variety of flows. The range of flow is usually from very hard to very soft. The degrees of hardness or softness are designated by letters with subscripts, such as $H_8, H_7 \ldots\ldots M \ldots\ldots S_5, S_6$. Each formulation has a definite set of physical properties. Each degree of flow in any one formulation differs in physical properties from another. Definitions of physical properties are given at the foot of Table 6-3. For example, in the case of a welding type formula, in going from a hard to a soft material, the elongation increases and the tensile strength, compressive strength, and flexural strength decrease. The softer the material, the greater the moisture resistance and the lower the surface hardness. In comparing flow degrees of different formulas, there is a great deal of overlapping of values. This crossing of similar values in different flows is very important, since the choice of material for a particular application is dependent upon it. Material manufacturers list the numerical values for various properties in each flow for each formulation. These lists are published and are available upon request from the manufacturer. A condensed chart for illustrative purposes is shown in Table 6-3.

A comparison of the physical properties of four different formulas in the same flow in Table 6-3 shows many differences. While one type may be superior in the mechanical strengths, it is

TABLE 6-3

PHYSICAL PROPERTIES OF SOME INJECTION-TYPE ACETATE MOLDING COMPOUNDS

Formula	Degree of Flow	Flow Temperature Degrees F	Per Cent Elongation	Tensile Strength* Pounds per Square Inch	Flexural Strength* Pounds per Square Inch	Impact Strength Izod Test* Foot-Pounds per Inch of Notch	Per Cent Water Absorption	Rockwell Hardness*
General	H_4	330	8	8,300	14,500	.8	3.4	95
General	M	293	13	5,800	9,600	1.4	3.2	70
General	S_2	272	15	4,700	7,100	1.9	3.1	55
Physical	H_4	330	11	9,100	16,000	.9	2.6	103
Physical	M	293	20	6,400	10,100	1.6	2.2	78
Physical	S_2	270	26	5,000	7,500	2.4	1.9	63
Mechanical	H_4	Not manufactured in this flow.						
Mechanical	M	295	6	8,500	15,500	.9	2.8	94
Mechanical	S_2	275	8	6,700	12,000	1.2	2.7	83
Welding	H_4	330	15	8,000	13,500	1.2	2.7	93
Welding	M	293	31	5,200	8,100	2.1	2.6	65
Welding	S_2	275	42	3,900	5,400	3.0	2.3	48

*Definitions—
Tensile strength—the tearing strength of a material.
Flexural strength—the actual breaking strength of a material.
Izod Test—A hammer is struck against a notched test specimen under specified conditions, to test impact strength.
Rockwell Hardness—A surface hardness test in which a steel ball is pressed against a specimen; and the resultant indentation is measured.

definitely inferior to some other formula in some other characteristics. In choosing a formula for a particular application, these values must be closely studied. Choose *first* the degree of flow required by the size, shape, and type of the article to be manufactured. Consideration is also given to molding pressure when choosing the degree of flow; since it is this pressure that forces the material to move. Once the practical flow has been established, the other physical properties of the article must be gone into in detail. Does the article require high impact strength or simply good surface hardness? Is chemical resistance or heat resistance the most important quality of the molded article? With these properties in mind, the charts for the various formulas are studied in relation to each other for the particular flow that has been chosen. The formula to choose is the one giving the best combination of values. It will be noted that under the injection-mechanical type of formula the material is not manufactured in the H_4 flow. This may be taken to mean either that the material at that hardness would be too hard to mold or that the elongation value would be so low as to make the article too brittle.

6-14. Factors Related to Flow.—The flow value of any acetate material is determined by the plasticizer content. In phenolics, it is the binder that influences the degree of flow. Since cellulose acetate is thermoplastic, it does not go through any A-, B-, or C-stage. The main reason for adding plasticizer is to lower the softening point of the cellulose acetate. The decrease in softening-point temperature is directly proportional to the amount of plasticizer used. Each plasticizer has a different lowering effect. In some cases, 1 per cent of plasticizer will lower the softening temperature 1 degree whereas it may take 5 per cent of some other plasticizer to lower the softening temperature of the same flake 1 degree. The rolling operations are important because they knead the plasticizer with the flake. Too long a rolling or mixing operation may result in loss of plasticizer with a resultant change in flow.

As the flow increases in hardness, the plastic softening temperature (flow temperature, Table 6-3) increases. The higher the softening point of the compound, the quicker is the "set." Therefore, the degree of flow enters into the calculations of the molding cycle; that is, the time it will take to complete a molded product, taking into consideration the time for softening, injection or com-

pression, cooling, and removal from the mold. It is advantageous, wherever the physical properties permit, to use the hardest flow possible.

6-15. Mottling and Graining.—All types of mottle and grain effects are possible with cellulose acetate. There are two methods that can be used to produce articles of this kind. The consumer can make the mottle by blending different-colored molding powders. Introduction of the blend into the molding operation will produce a mottled article. To produce graining, materials of several different colors and of different flows are blended together. The flows must be at least five degrees removed from one another. This difference in flow will allow the softer material to flow around the harder material. If the flows are too close, they will mingle together and produce a mottled rather than a grained effect. The manufacturer sometimes makes the mottle or grain by blending the desired materials and putting them through the rolls. The rolled sheets or chunks are then put through the pulverizer. The resultant granules are multicolored.

6-16. Reuse of Material.—Thermoplastics have a natural advantage over thermosetting compounds in that there is practically no waste. All scrap and rejected articles can be ground up and used again without having to be reprocessed. Naturally, there are limitations as to reuse. Continuous regrinding and using of scrap material will cause it to deteriorate. Deterioration is due to the fact that, through continued heating in the molding operation, the plasticizer will have been volatilized. In order to prevent this, it is common practice to blend the ground scrap with new molding compound. In this way, the loss of plasticizer is not appreciable. The colors of the reused and the new materials must be closely matched. If, for instance, the color is a light pastel made from an unstable rhodamine dyestuff, the color will change in the first molding operation because of the heat developed in that operation. This material, when reground, cannot be blended with new material, as a mottle would result.

6-17. Formulas and Applications.—In the acetate plastics, the cellulose acts both as binder and as filler. Plasticizers are present in varying amounts and types, the selections depending on the

flow and the characteristics to be obtained. Oil-soluble and spirit-soluble dyes are used where transparency or translucency is desired. Opacity is obtained by the use of earth pigments. For color effects like fluorescence and phosphorescence, such special agents as zinc sulfide and rhodamine dyestuffs are used. Complete lines of colors in transparents, translucents, and opaques are available in acetate molding powders. Since acetates are thermoplastic, no accelerator or retarder is required. There is no lubricant in cellulose acetate as such, but the plasticizer may be thought of as fulfilling that function because of its natural slipperiness.

To illustrate the many types of formulations, the following two formulas are given for the sake of comparison:

		Per Cent
A. Binder and filler	(cellulose acetate)	65
Plasticizer	(tributyl phosphate,	18
	dimethyl phthalate)	16
Color	(pigment or soluble dye)	1
B. Binder and filler	(cellulose acetate)	67
Plasticizer	(methyl phthalyl ethyl glycollate,	22
	triphenyl phosphate)	10
Color	(pigment or soluble dye)	1

The first formula provides toughness and water resistance; the second is preferable for water-proofness and flame-proofness.

Cellulose acetate is known to the trade as Fibestos, Lumarith, Tenite, Nixonite, Plastacele, and Bakelite Cellulose Acetate. It may be obtained in the form of granules, pellets, film, rods, sheets and tubes. Buttons, tool handles, lenses, frames, fish lures, instrument panels, cases, combs, knobs, stripping for furniture, and the like are made by compression, injection, extrusion, and blow molding. Cellulose acetate can be formed, sawed, drilled, turned, and milled.

6-18. Plastic Glazing.—Casualties caused by flying glass fragments during an explosion are usually greater than injuries from other causes. Safety glass reduces the flying-glass hazard; but, because of its high cost in large sections, the applications are somewhat limited. It remained for the plastic industry to develop

and market a new type of safety glass known as plastic glaze. The term *plastic glazing* is given to any plastics substitute for glass.

There are several types of plastic glazing; the two most important ones are sheet glaze and dip glaze. In the sheet-glaze process, sixteen-mesh wire is sandwiched between sheets of .015-inch clear cellulose acetate. By hot pressing the two sheets, the wire mesh is firmly sealed between them. Both top and bottom surfaces remain smooth. The dip-glaze process takes fourteen-mesh wire and immerses it in a heavy solution of cellulose acetate. When the product is removed from the bath and dried of solvent, the acetate forms a continuous film over the interstices of the wire. Both top and bottom surfaces are corrugated.

The bursting strength of these glazing materials is 200 pounds per square inch. Owing to the presence of the wire, perfectly clear vision is not obtained, because light is transmitted to the extent of only about 60 per cent. The outlines of images are easily seen through the plastic material, but the details are not distinct. Plastic glazing finds extensive application as windows in shell-loading and munitions plants. This material has an ultra-violet-ray transmission of about 45 per cent, and, as a consequence, is used in greenhouses and solaria. Vimlite and Lumapane are trade names for plastic glazing products.

6-19. Other Uses.—Cellulose acetate finds extensive use in the paint, lacquer, and textile industries. Its use in these industries will be given separate treatment. However, acetate is used to a great extent in the manufacturing of seamless containers. While this is no form of pressure molding, it can be classed as molding with some reservation. Flakes of material with high acetyl content are dissolved in a special mixture of solvents, and the resulting solution is brought to the proper viscosity. A metal or wooden master model is dipped into this solution. By very slowly withdrawing the model, a film of the solution adheres. Air drying evaporates the solvent and leaves a tough acetate film on the form. This film, when treated with hot water or live steam, can be removed as a single replica of the model.

Generally, a series of master models are mounted together and are dipped as a single unit. Most of the containers for styptic pencils and toothbrushes are made by this method. The thickness of the container will depend on the number of dippings. By adding

a soluble dyestuff to the solution, a color variety is obtained. Air bubbles that may find their way into the solution must be avoided, so as to insure good finished products. To guard against air bubbles, the dipping tank is usually sealed and is placed under partial vacuum. Another precaution is regularity of dipping to maintain uniform thickness of the film. Too rapid withdrawal causes the solution to run, and results in heavy spots. The dipping of the mold in the solution is done by machine; thus, a steadiness and uniformity that is lacking in the human hand is insured.

Polystyrene

6-20. Chemistry.—Polystyrene is a thermoplastic synthetic resin of the vinyl group. As the name implies, it is a polymerized product of styrene. Its use as a plastic material has been known for a long time, but was restricted because of preparation difficulties. In chemical terminology, styrene may also be called vinylbenzene—a benzene nucleus to which is attached a vinyl grouping ($—CH{=}CH_2$).

The starting material in the production of polystyrene resin is monomeric styrene, which is a colorless, oily liquid that boils at 143° C. There are many ways in which styrene can be produced. The conversion of such a liquid into a resinous solid depends on the time, the temperature, and the catalytic agents employed. Resins of different properties are made by varying these factors.

Styrene contains carbon atoms in the vinyl group which are capable of attaching to other molecules through the double bond. Therefore, polymerization simply means constructing a chain of these molecules by linking them together. A simple arrangement would be a long chain of methylene groups in alternate molecules of which phenyl is substituted for one of the atoms of hydrogen, as shown in Fig. 6-6.

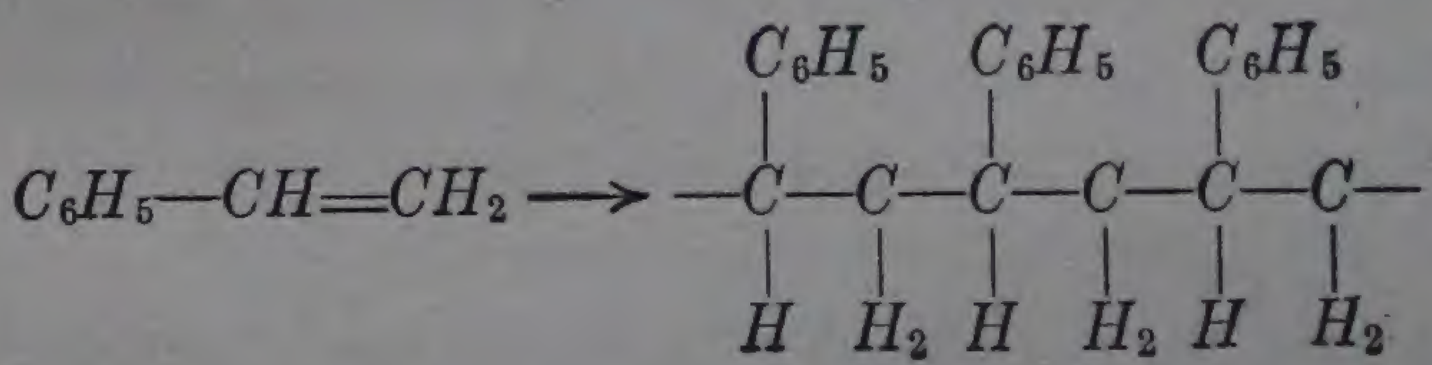


Fig. 6-6. Polymerization of Polystyrene.

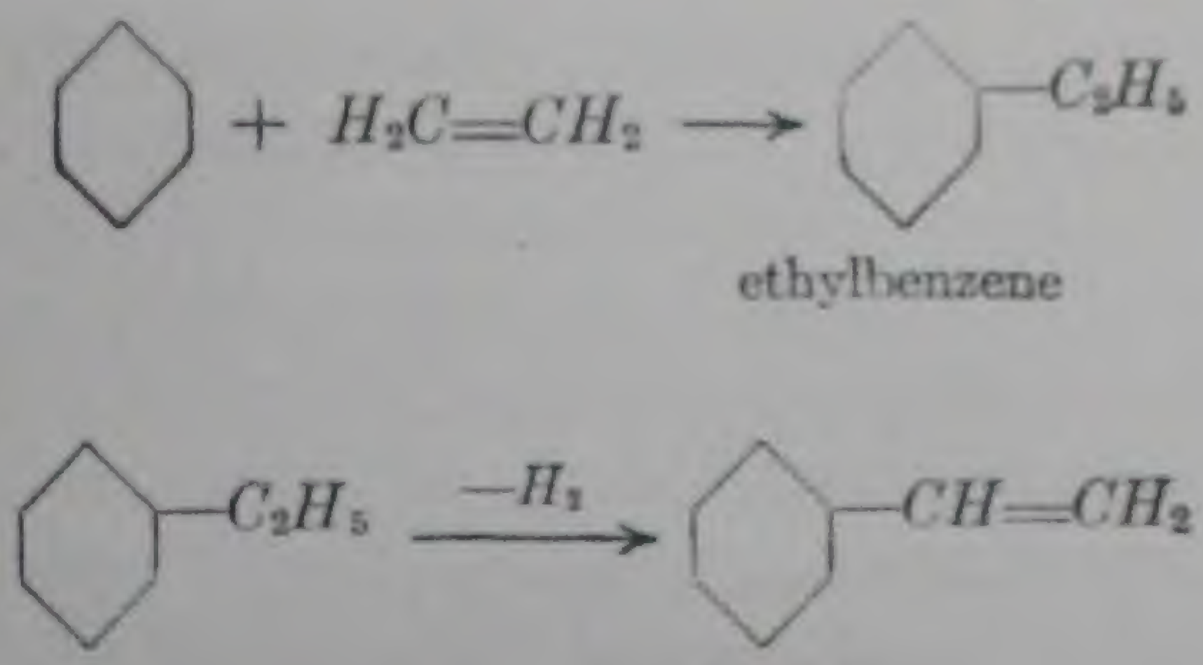


Fig. 6-7. Preparation of Styrene.

6-21. Preparation of Styrene.—The impetus given the manufacture of synthetic rubber, which utilizes styrene as a basic material, has improved the methods of manufacturing styrene. Benzene, an oily liquid obtained from coal or petroleum, and ethylene, a gas also derived from coal or petroleum, are starting materials. When benzene is reacted with ethylene, ethylbenzene is formed. By removing 2 hydrogen atoms, ethylbenzene is converted to styrene. The reactions to show the preparation of styrene are represented in Fig. 6-7.

Styrene is found in coal tar in small amounts. Until it is possible to recover styrene from coal tar economically, the chemical will continue to be made synthetically from ethylene and benzene. Investigations on the coal-tar products have made progress and may eventually lead to the development of a commercial source of styrene.

6-22. Manufacture of Polystyrene Resin.—In the manufacture of polystyrene resin, ethylene is passed into benzene liquid in the presence of a metallic catalyst such as aluminum chloride. The reaction takes place readily in an ordinary mixing kettle. Ethylbenzene has two more hydrogen atoms per molecule than styrene. When these two atoms are removed by running the ethylbenzene through an iron tube at approximately 700° C, the ethylbenzene is dehydrogenated, with the formation of liquid styrene. Styrene polymerizes so easily that control of the reaction is difficult. Styrene polymerizes almost spontaneously. Light and a small amount of heat are enough to start polymerization. Impurities, such as dirt, will start it also. Agitation of any form is to be avoided, since it chemically excites styrene. Fast polymerization produces a short-chain compound, whereas slow polymerization

produces a long-chain compound. Although both products are identical in appearance, they have different chemical and physical properties.

The molecular weight of styrene is 104. Molecular weights of polystyrenes vary upward to 140,000. This means that the higher polymers of styrene have as many as 1,350 linked styrene molecules. While all investigators do not agree on the structural formula of the polymer, the consensus seems to be that it is in general a straight-chain arrangement. Impurities may cause cross-linkage or, if the polymerization takes place too fast, the linkage may be forced to cross.

Styrene is usually polymerized by means of heat. It can be polymerized in solution by the use of a catalyst, but after polymerization it is difficult to remove the solvent and the catalyst. To produce a polymer by heat, the styrene monomer is placed in a closed kettle and its temperature is raised. The monomer soon starts to thicken. This thickening is an indication that the chain is forming and the molecular weight is increasing. The slower the heating, the more gradual the polymerization. Although polystyrene requires no plasticizer, it is supplied in several grades of flow. This variation in flow is obtained by control of the molecular weight and molecular distribution. Polystrene for injection molding has a molecular weight ranging from 70,000 to 140,000. The higher the weight, the harder the compound; the lower the weight, the softer the compound.

The boiling point of liquid styrene is 292° F; so polymerization temperatures should never exceed 280° F. The polymerization reaction is so highly exothermic that the temperature must be very carefully controlled. In converting from the monomer to the polymer, there is a decrease in volume, which results in a change in the specific gravity of the material. There is always a tendency to form voids in the polymerization process because of this change in volume. If the conditions are well controlled, the voids in the finished resin will not be present. Voids show themselves as air bubbles.

Styrene resin depolymerizes at about 572° F. Experiments have shown that styrene polymerized above 280° F is very brittle and is almost useless as a molding compound. The usual procedure is to bring the temperature up to about 275° F very gradually. When the solution has reached the consistency of molasses, the

heat is reduced to about 150° F and the material is allowed to stand. After several days of standing, there results a hard, crystal-clear solid, which is polystyrene. To facilitate handling, the material is usually poured into shallow trays for the standing period at 150° F. It is much easier to grind the material to molding-powder size if the resin is in a thin layer rather than a thick block. The resin, upon cooling to room temperature, is put through a rotary cutter that produces a granular molding powder.

6-23. Manufacture of Molding Powders.—In Fig. 6-8 is shown a flow chart for the production of polystyrene molding compounds. Polystyrene is produced only in a crystal-clear material by the heat-polymerization process. To obtain a complete range of colors, processing of the polymer is necessary. Attempts have been made to color the liquid styrene prior to polymerization, but they have failed for several reasons. For one thing, the dyestuffs interfered with the polymerization process and, as a result, no control over weight or chain formation could be had. Secondly, the colors were unpredictable, as the dyestuff would not hold its color throughout the process.

Color is applied to polystyrene by a calender-roll process. The polymer is ground rather fine and is placed on the rolls. The heat imparted by the rolls causes the material to soften and form a coating on the colder of the two rolls. The rolls are of the same types as those used for phenolics. As shown in Fig. 6-9, a mechanical knife removes the coating from the roll while polystyrene is being compounded with color. The rolls are geared for different speeds and have a heating differential of about 100 degrees F. Since styrene needs no lubricant, plasticizer, or accelerating agent, the only addition is color which is dissolved or dispersed in a solvent compatible with polystyrene. The material is cut away from the roll by a mechanical or a hand knife and is re-fed to the rolls, this process being continued until the color is uniform throughout the mix. Finally, the material is removed and, when cool, is broken into chunks, as shown in Fig. 6-10. These chunks are put through a rotary cutter to reduce them to a molding powder.

The heat of the milling operation continues the polymerization of the polystyrene. For this reason, polystrene that is to be colored is incompletely polymerized in the reacting kettle, the polymerization being completed by the heat of the milling operation. If

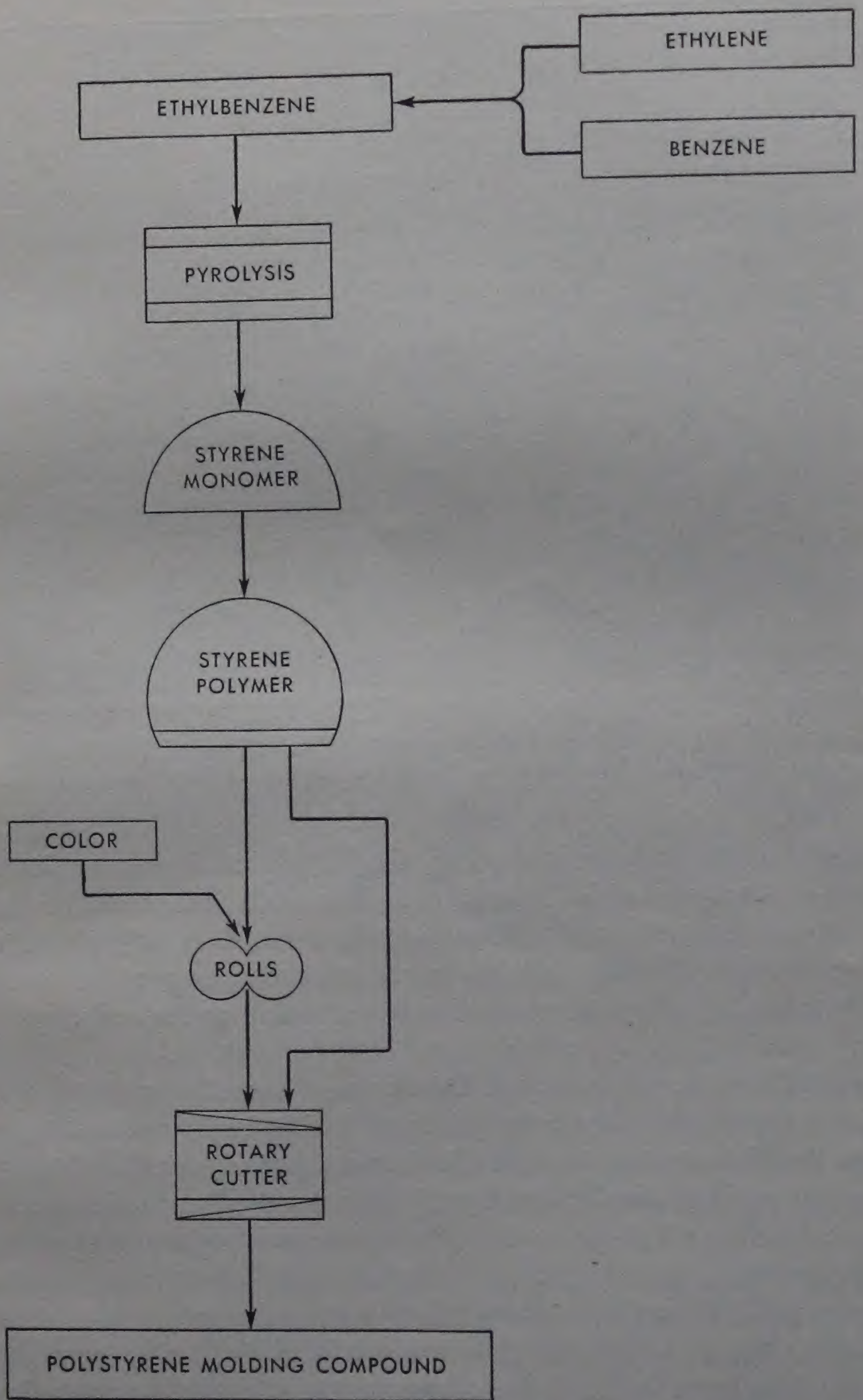
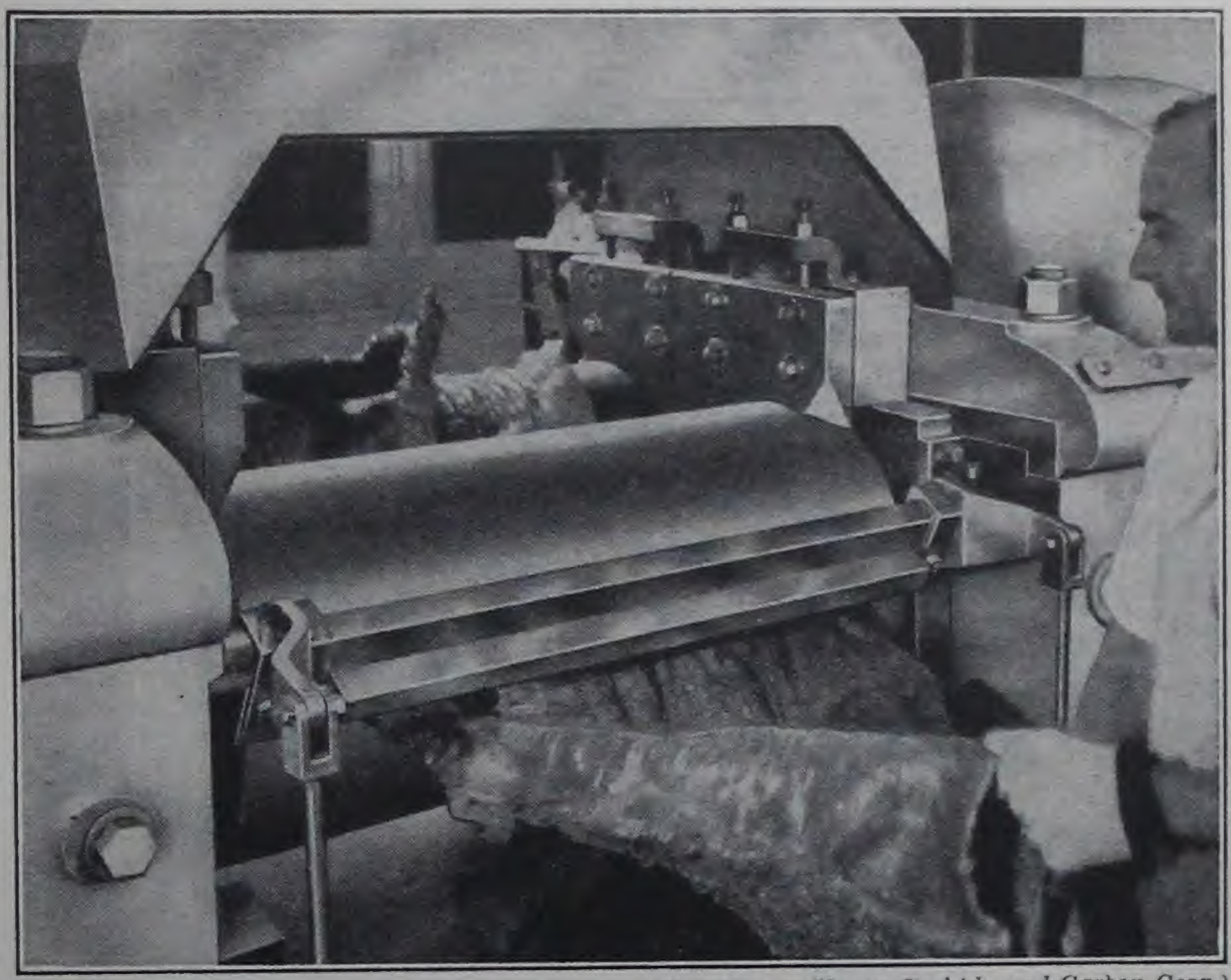


Fig. 6-8. Flow Chart for Polystyrene Molding Compounds.



(Courtesy of Union Carbide and Carbon Corp.)

Fig. 6-9. Calender Rolls for Compounding Polystyrene With Coloring Agents, Showing Mechanical Knife for Cutting Sheet Away From Rolls.

polystyrene is to be crystal clear, the polymerization is completed in the reacting kettle. Polystyrene is ground into fines for the color-rolling operation, because it is difficult to soften large granules on the rolls. Besides ease of operation, the fines provide much better control of the amount of polymerization on the rolls.

6-24. Other Polystyrene Products.—Generally speaking, the vinyls—including polystyrene, vinyl chloride, and vinyl acetate—and the acrylates are the most difficult compounds to roll. Of these, styrene is about the hardest to roll. Polystyrene is sold as rod and tube stock, as well as molding powder. Rod and tube stock is produced on a continuous-extrusion machine. Polystyrene is sometimes sold in block form, in which case it is polymerized as a block rather than being molded or extruded. It is possible to pour the liquid monomer into a crude shape and to allow it to polymerize in the shape itself. This procedure is similar to the casting of resins, but the amount of it being done is very small. Where any volume is concerned, it is cheaper to mold than to cast.

(Courtesy of Union Carbide and Carbon Corp.)

Fig. 6-10. Breaking Up Sheets of Rolled Polystyrene.

6-25. Prevention of Polymerization.—Styrene monomer has such a decided tendency to polymerize spontaneously that it is necessary to add inhibitors to stabilize styrene that is not to be used immediately. Inhibitors, which are not to be confused with retarders, are used to prevent a reaction from taking place. Before the styrene can be used, the inhibitor must be removed, as polymerization cannot take place as long as the inhibitor is present. Sulfur and hydroquinone are good inhibitors. About .5 per cent of inhibitor is required to prevent polymerization. The inhibitor is removed by adding 1 per cent of sodium hydroxide and vacuum-distilling the mixture. The boiling point of styrene at a vacuum equivalent to 28 inches of mercury is about 150° F. The first few milliliters of the distilled liquid should be discarded, since they will contain water.

6-26. Theory of Integral Plasticization.—The function of a plasticizer is to make a material flow more easily and uniformly. It accomplishes this function by filling in the void spaces between molecules. In most instances, a plasticizing agent is added to a plastic material, but there are cases in which groups of atoms in the compounds themselves fulfil the function of a plasticizer. The phenyl groups of polystyrene act as plasticizing agent. The structural formula of chemicals, as for example the hexagon to designate benzene, does not give a true picture and is only used to simplify the language of chemistry. The polystyrene molecule is a space molecule and exists in three dimensions. It is not beyond imagination, then, to picture the phenyl groups in the long polystyrene chain as filling in the void spaces between molecules. In so doing, the various individual parts of the chain can easily slide by one another. It must also be remembered that the chain is not rigid, but is flexible like a watch chain. It may twist and turn in all directions.

6-27. Formulation.—Like urea, but unlike the phenolics and acetates, styrene usually is made in one formulation. To incorporate fillers in polystyrene would destroy one of its best properties—transparency. The monomer styrene finds a good outlet in the adhesive and synthetic-coating fields. It is usually mixed with suitable solvents and dyestuffs to form a solution that can be applied as a coating.

Polystyrene is often called organic glass because of its good light transmission. Molded articles, when dropped, have a metallic tinkling sound that is unmistakable. The molding compound, as sold, is practically pure resin with a small addition of coloring matter. For certain difficult molding applications, a small amount of lubricant is used, but this practice is the exception rather than the rule. Coloring matter that is to be added to polystyrene is dispersed or dissolved in hydrocarbon solvents, because the resin is soluble in most hydrocarbons. When the solvent is compatible with both the coloring matter and the binder, a uniform coloration can always be expected.

As far as the six basic ingredients of a plastic are concerned, their functions are filled by only two substances. Polystyrene acts as the binder, plasticizer, and lubricant. Since polystyrene is thermoplastic, no accelerator or retarder need be used. In some

cases, an inhibitor is used to prevent polymerization, but it must be removed before the material can be used. Certain vat and naphthol dyes, lake toners, and inorganic pigments, either separately or in combination, have been found satisfactory as coloring agents for use with polystyrene. A typical formula, therefore, would be 98 per cent of resin and 2 per cent of dye.

6-28. Applications.—Polystyrene possesses some of the best properties desired in any plastic material. Among these properties may be mentioned chemical resistance, high dielectric strength, high resistance to the passage of electricity, little or no water absorption, low specific gravity, and high index of refraction. Since the material is thermoplastic, injection molding is the most economical method of handling polystyrene. Loalin, Lustron, Styron, and Bakelite Polystyrene are trade names of polystyrene plastics.

One of the early uses of polystyrene was for dental plates. The plastic is dimensionally stable, odorless, tasteless, and resistant to the attack of acids and alkalies—even hydrofluoric acid, which is capable of dissolving glass. Stoppers of containers for many corrosive chemicals are made of styrene by injection molding. Liquid pour-outs, bar accessories, and food containers are other uses. Foils and rods employed in radio and electronics give highly satisfactory performance under all frequencies and all conditions of humidity. Jewelry, varnishes and coatings, television accessories, and illuminated signs and panels are promising fields for the application of polystyrene.

Acrylic Resins

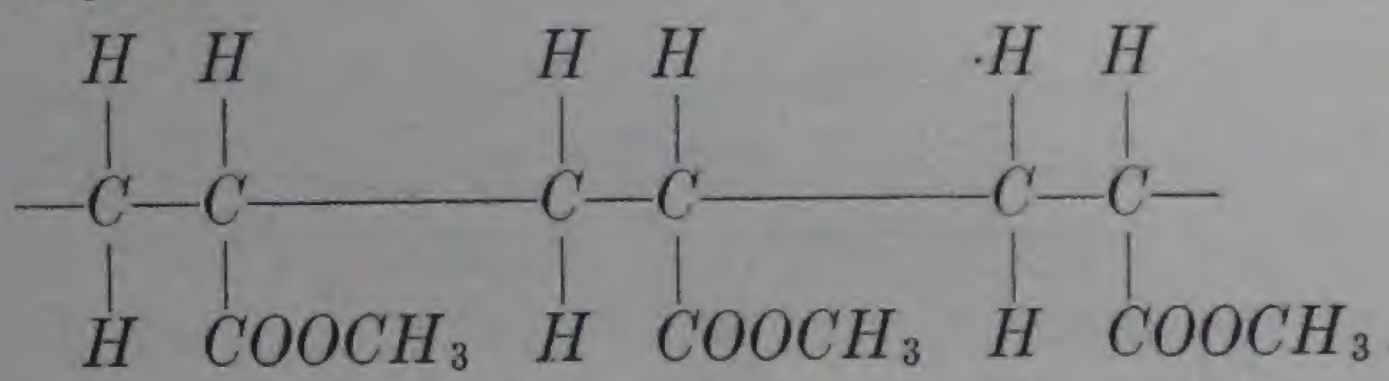
6-29. Introduction.—All the acrylic resins are classified as thermoplastics of the synthetic-resin type. Since they contain the vinyl group, they are also classed as vinyl resins. The raw materials used in the manufacture of acrylics are common ones; thus, these resins are called coal-air-water plastics.

6-30. Acrylate Polymer.—Esterification is the process of producing an ester by combining an acid and an alcohol. Acrylic acid, when esterified with methyl alcohol, produces methyl acrylate, which is capable of polymerizing. Methyl acrylate is a colorless liquid which is lighter than water and boils at 80.3° C.

As in the case of styrene, polymerization of methyl acrylate involves the formation of long-chain units. Therefore, by taking methyl acrylate in its monomeric form and exposing it to proper conditions of temperature and catalyst, a polymer forms, as shown in Fig. 6-11.

$CH_2{=}CH{-}COOCH_3 \longrightarrow$

Methyl acrylate



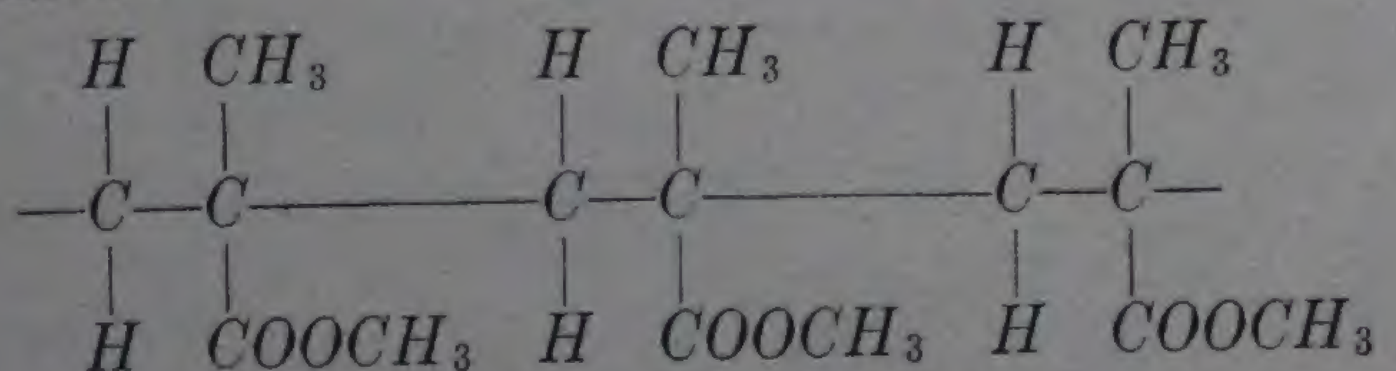
methyl acrylate polymer

Fig. 6-11. Polymerization of Methyl Acrylate.

6-31. Methacrylate Polymer.—Any number of esters can be derived from acrylic or methacrylic acid. The most important one, however, is methyl methacrylate, which polymerizes into a clear resin of exceptional properties. The structure of this polymer is shown in Fig. 6-12. It is a basic methyl acrylate polymer with a methyl group substituted for hydrogen in alternate carbon

$CH_2{=}CCH_3{-}COOCH_3 \longrightarrow$

methyl methacrylate monomer



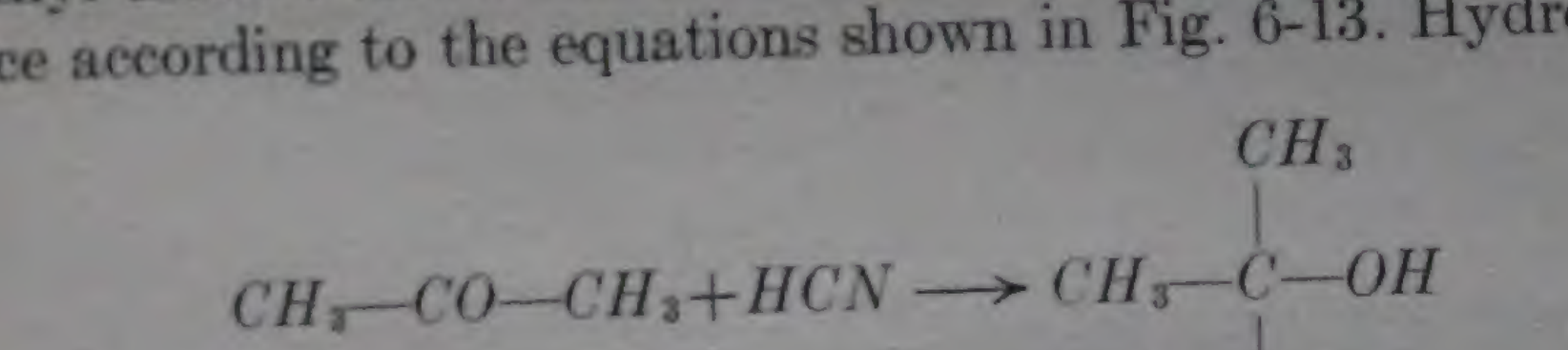
methyl methacrylate polymer

Fig. 6-12. Polymerization of Methyl Methacrylate.

atoms. These chain polymers can satisfy their end valences by taking on other substances or by forming a ring compound. The manufacturing technique determines which process is involved.

6-32. Methacrylic-Acid Ester.—The methyl ester of methacrylic acid has become the most popular of the methacrylic esters in use in the United States for plastic materials. Moreover, the production of methacrylates can draw from the petroleum, agricultural, or synthetic industries for its raw materials. Acetone, a starting material, can be obtained from the fermentation of carbo-

hydrates or the action of heat on acetic-acid salts. A commercial practice is the conversion of propylene to its corresponding alcohol, which, upon oxidation, yields acetone, as shown in the following equation:



Acetone is acted upon by hydrocyanic acid, which converts it to acetone cyanohydrin; further processing with sulfuric acid and methyl alcohol forms the methacrylate ester. The reactions take place according to the equations shown in Fig. 6-13. Hydrocyanic

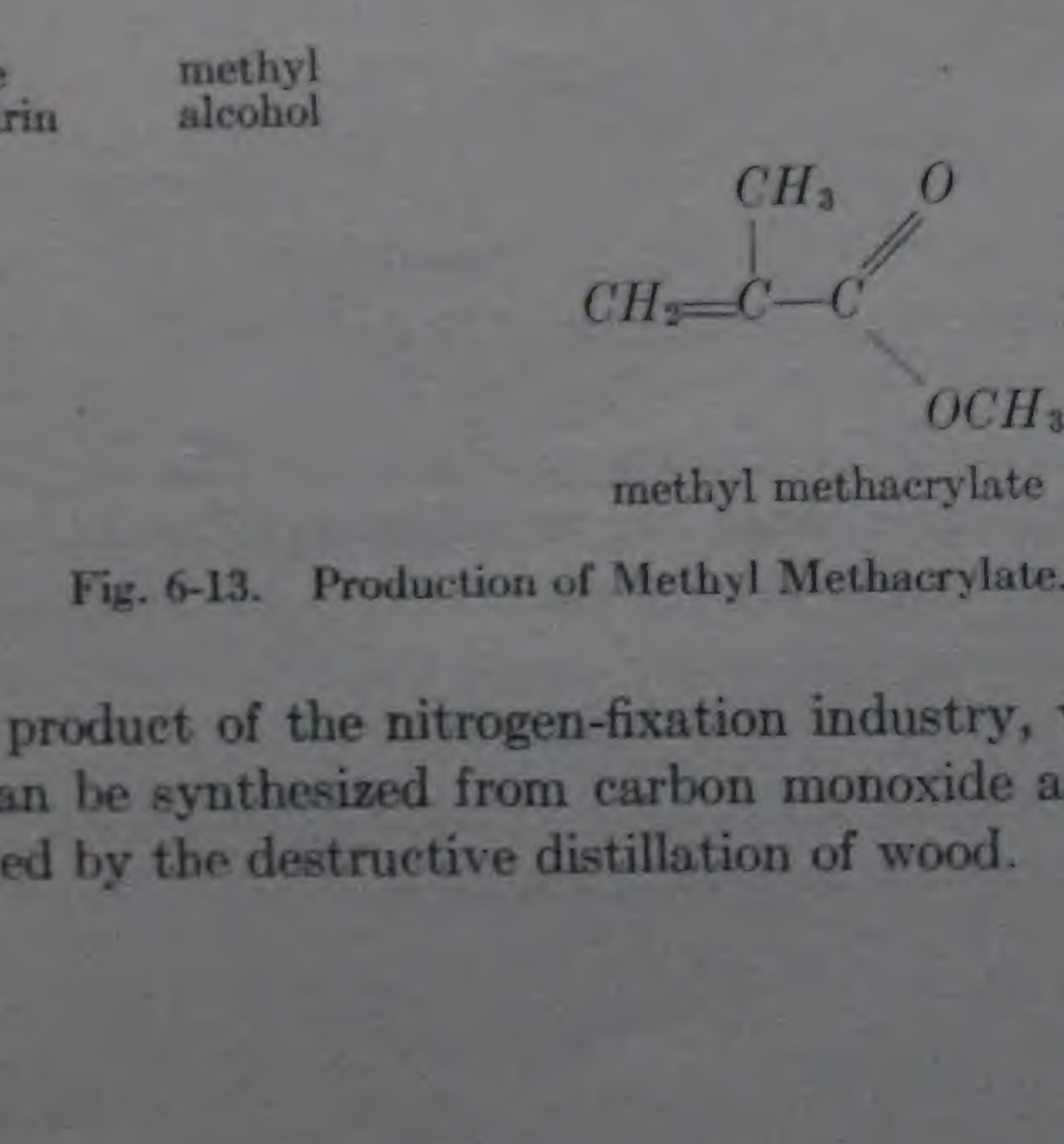


Fig. 6-13. Production of Methyl Methacrylate.

acid is a product of the nitrogen-fixation industry, while methyl alcohol can be synthesized from carbon monoxide and hydrogen or obtained by the destructive distillation of wood.

6-33. Acrylic-Acid Ester.—Receiving more favorable attention in Europe than in the United States, the acrylic-acid esters are well-known plastics. Although the starting materials are different from those used in making the methacrylates, the chemical steps are somewhat the same. When ethylene, which is a product of petroleum cracking or ethyl-alcohol dehydration, is passed through a solution of chlorine and water, ethylene chlorohydrin is formed. This reaction product combines with sodium cyanide to produce ethylene cyanohydrin, which with methyl alcohol and sulfuric acid forms the methyl-acrylate monomer, as shown in stepwise fashion by the equations in Fig. 6-14.

Fig. 6-14. Production of Methyl Acrylate.

6-34. Factors Affecting Polymerization.—The acrylic derivatives, like those of styrene, are manufactured in two steps. The first step is the formation of the monomer liquid, and the second is the polymerization process. The flow chart in Fig. 6-15 shows the production of two acrylic resins.

The monomer liquid is made by reacting molecular quantities of the raw materials in a reaction kettle under controlled tem-

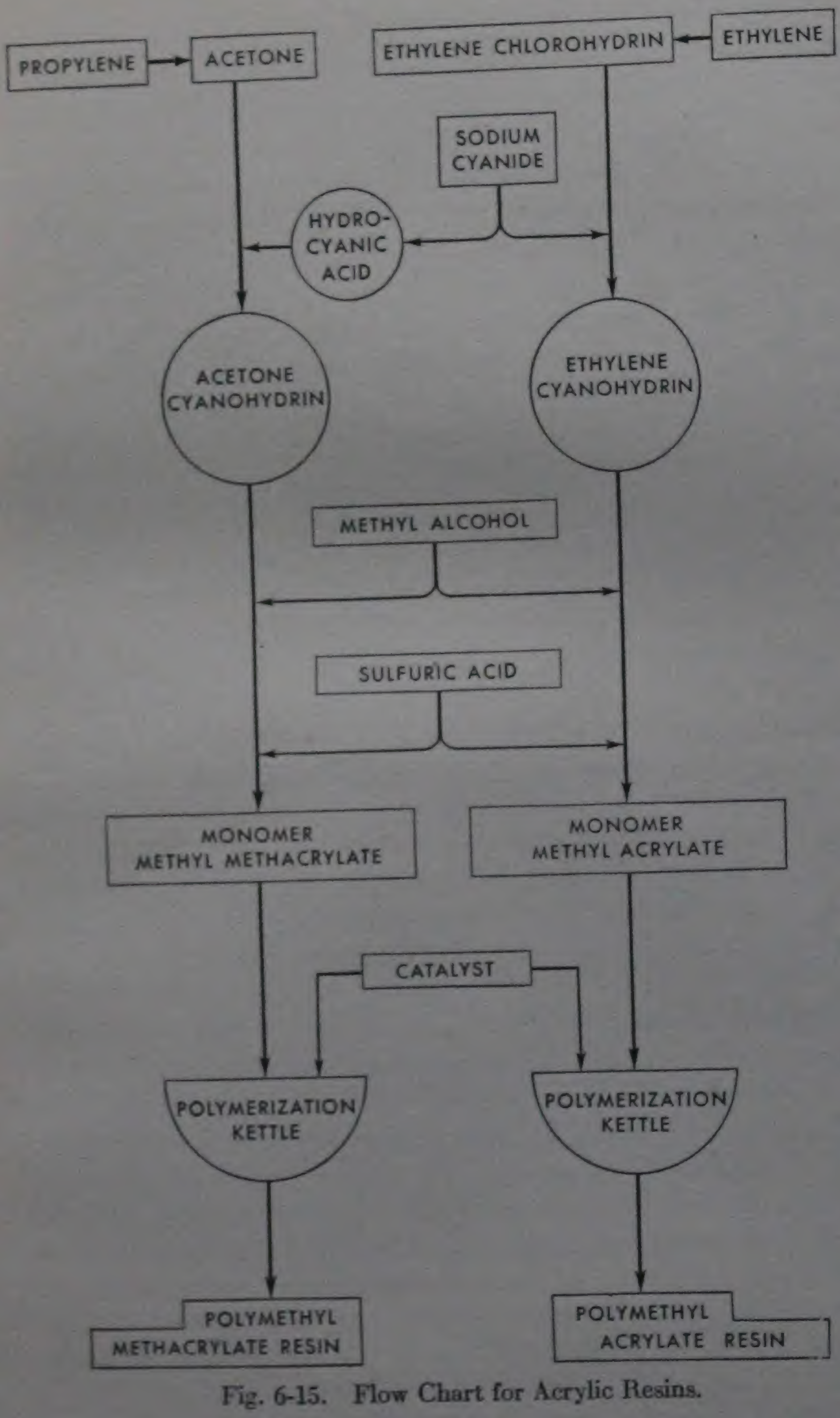


Fig. 6-15. Flow Chart for Acrylic Resins.

perature conditions. Before they are ready for polymerization, the esters are subjected to fractional distillation to separate them from unreacted products. They are also filtered, as impurities hinder polymerization.

Acrylics polymerize more quickly than methacrylics. Any oxygen-containing substance seems to have the property of inducing polymerization, peroxides being excellent catalysts for polymerization. The change from the monomer to the polymer is strongly exothermic, the heat of reaction being about 80 calories per gram. For this reason the conditions of polymerization must be rigidly controlled, as this amount of heat, if it were allowed free rein, would raise the temperature to a point where the monomer would vaporize and produce bubbles. Best practice is to polymerize at a rate that allows the heat to be dissipated as fast as it is formed.

Since the boiling point of the methacrylate is about 215° F, the polymerization temperature should never exceed this point. There must be constant agitation throughout the reaction. The molecular weight of the polymer, like that of styrene, is the controlling factor of the properties of the compounds to be formed. No plasticizer or lubricant is used in the manufacturing process. The acrylics are produced as cast sheets and blocks, as well as molding powder. If the material is to be cast, the polymerization is continued until the resin thickens but will still be fluid enough to fill a mold. The sheets or blocks are then placed in a conditioner and kept at 110° F until complete hardening takes place.

6-35. Molding Powder.—If a molding compound is to be made, the emulsion-polymerization method is used. In this process, the monomer is finely dispersed in water and is allowed to polymerize. The polymer is precipitated as fine beads, instead of as a thick syrupy resin. The beads are separated from most of the water by a centrifugal drier. The wet beads are placed in a perforated basket which is made to revolve at such a high speed that the beads are dried by forcing the water out of them through the perforations. Such a machine, known as a basket type centrifuge, is shown in Fig. 6-17. The granules are usually passed through a rotary drying oven to remove any moisture that may still be present. The very fine particles are further processed with color on calender rolls.

(Courtesy of E. I. du Pont de Nemours Co.)

Fig. 6-16. Basket Type Centrifuge for Removal of Moisture From Polymerized Methyl-Methacrylate Powder.

The precipitation method of forming the polymer is not absolutely necessary, but it is claimed that a better molding compound is obtained when it is used. Another method is to pour the heated resin into shallow trays and allow it to cool. When sufficiently cold, the resin is broken into small chunks that are suitable for the rolling process.

The rolling of a clear methacrylate is a rather simple procedure, as there are no other ingredients, except color, to be added. Rolling densifies the material, making it more suitable as a molding compound. The fines or chunks, whichever are used, are placed on hot calender rolls. The heat of the rolls soon softens the material, and a coating forms on the cooler roll. The coloring matter, dispersed in suitable solvent, is added to the softened material and is thoroughly kneaded into the mass by manipulation of the knife. When uniformity is achieved, the sheet is cut away from the rolls and allowed to cool. It is then broken and put through a rotary cutter to reduce the methacrylate polymer to molding granules.

The flow of the molding compounds can be controlled by regulating the degree of polymerization. The molecular weight of the methyl methacrylate monomer is 100. A good polymer consists of about 1,000 well-linked monomer molecules. The greater the number of monomer molecules that make up the polymer molecule, the harder the compound. In the rolling operation heat must be controlled so as not to polymerize the compound too far. There is no A-, B-, or C-stage in the formation of acrylic or methacrylic plastic materials.

6-36. Formulation.—No plasticizers are necessary in the molding-compound formulation, because the $OOCH_3$ groups of the polymer structure act as integral plasticizers. Such compounds are usually 100 per cent resin. No basic fillers are used, since their function is fulfilled by the resin. The monomer needs stabilization to prevent spontaneous polymerization. A small amount of hydroquinone provides this stabilization. When the monomer is to be used immediately, no inhibitor is needed; but, if the monomer is to be stored for any length of time, it is best to add an inhibitor.

A large amount of acrylic resin is used for casting around objects in order to preserve them. The dental and medical professions are fields in which this process is used to great advantage. The resin is usually supplied in liquid form with an inhibitor, which

(Courtesy of E. I. du Pont de Nemours Co.)

Fig. 6-13. Tongue Depressor With Lip Molded of Methacrylate Molding Powder.

is removed by vacuum distillation. The resin is polymerized in the casting.

A notable property of the acrylic and methacrylic resins is their ability to bend light around corners. If a rod is cast or bent into an S, light entering one end of the S will emerge from the other as a bundle of light. This property has been publicized as the new "edge lighting." The medical and dental instrument known as a tongue depressor, illustrated in Fig. 6-18, is a direct application of edge lighting.

Lubricants have been used with the acrylic plastics, but it has been found that they impair the optical properties of the product. The resins themselves are of a slippery nature and, in general, no lubricants are needed. In rare cases, where the shape of the article is intricate, a little lubricant might be used to ease the removal of the piece from the mold. In these cases, it will be found that optical clarity is not an important factor.

The acrylics are available in a complete range of colors from transparent crystal to opaque black. Odd color effects, such as fluorescence and phosphorescence, are also produced. Both dyestuffs and pigments may be used as coloring agents, although pigments cannot be used when any degree of transparency is required. Since color becomes an integral part of the compound, it is necessary that the color itself be compatible with the resin. Also, since the colors are dispersed in solvents, it is necessary that the solvent likewise be compatible with the resin. Best results are obtained by using lakes, toners, or oil-soluble dyes.

6-37. Properties and Applications.—The acrylics are superior in optical properties, ease of fabrication, dimensional stability, and chemical resistance. Acrylic molding powders may be molded by injection or compression, and the resins may be extruded into such forms as rods, tubes, and sheets. Attractive articles made from sheets and rods by means of machining, sawing, or heat forming have received wide acclaim. Transparent furniture and other articles of household and decorative value have been received with much enthusiasm by the public.

Cast acrylics are durable, light in weight, and flexible. They are used extensively in transparent enclosures for aircraft and in display housings. Cast sheets transmit the ultra-violet rays of the sun, whereas glass excludes these rays. Cast sheets are more resistant to chemicals than the acrylic sheet made from molding powder. Sheets are available in a variety of thicknesses and in sizes up to 27 square feet.

Optical properties of acrylics are exemplified by their application as spectacle glasses, camera lenses, magnifying lenses, highway reflectors, and light diffusers. Other applications for acrylic resin are in protective coatings, adhesives, impregnating varnishes, dentures, and as fillers for safety glass interlayers. Most of the lacquers and leather finishes have an acrylic, rather than a methacrylic, base. The methacrylate compounds find extensive use in the field of compression and injection molding. Lucite, Plexiglas, and Acryloid are trade names of acrylic-resin materials.

Chapter Seven

Other Thermoplastic Materials

Ethyl Cellulose

7-1. **Chemistry.**—Ethyl cellulose is a thermoplastic material which, although it is a cellulose derivative, is chemically different from other cellulose derivatives. The acetate and the nitrate of cellulose are esters, whereas ethyl cellulose is an ether. To put it another way, cellulose ether consists of cellulose molecules in which the hydroxyl groups in each cellobiose unit have been replaced by ethyl groups, C_2H_5-, instead of by acetate groups, $OOC \cdot CH_3$-, or nitrate groups, NO_3-, as in the case of esters. Inasmuch as the esters were prepared by allowing acids to react with cellulose, the first step in the preparation of ethyl cellulose is the reaction of a strong alkali, like sodium hydroxide, with cellulose. The product formed then is capable of being ethylated by ethyl chloride. The reactions that take place are represented by the equations in Fig. 7-1.

7-2. **Raw Materials.**—The sources of the cellulose used in the manufacture of ethyl cellulose are the same as for the cellulose esters. The cellulose must always be clean because impurities or dirt, although they will not affect the compounding, will ruin the appearance of the molded article. Sodium hydroxide, used in the first step in the production of ethyl cellulose, is a basic material of many industrial processes. It is made by the electrolytic decomposition of sodium chloride. Ethyl cloride, which is used to convert the alkali cellulose into its final form, can be obtained by subjecting ethylene, a refinery gas, to the action of hydrochloric acid. Ethyl cellulose then may be considered as manufactured from four common substances: salt, water, oil, and wood.

7-3. **Ethylation of Cellulose.**—A flow chart for the production of ethyl-cellulose plastics is shown in Fig. 7-2. Ethyl cellulose is produced by the reaction of ethyl chloride and alkali cellulose. Cotton linters derived from seed or wood that has been purified and bleached to pulp may be the source of cellulose. A measured

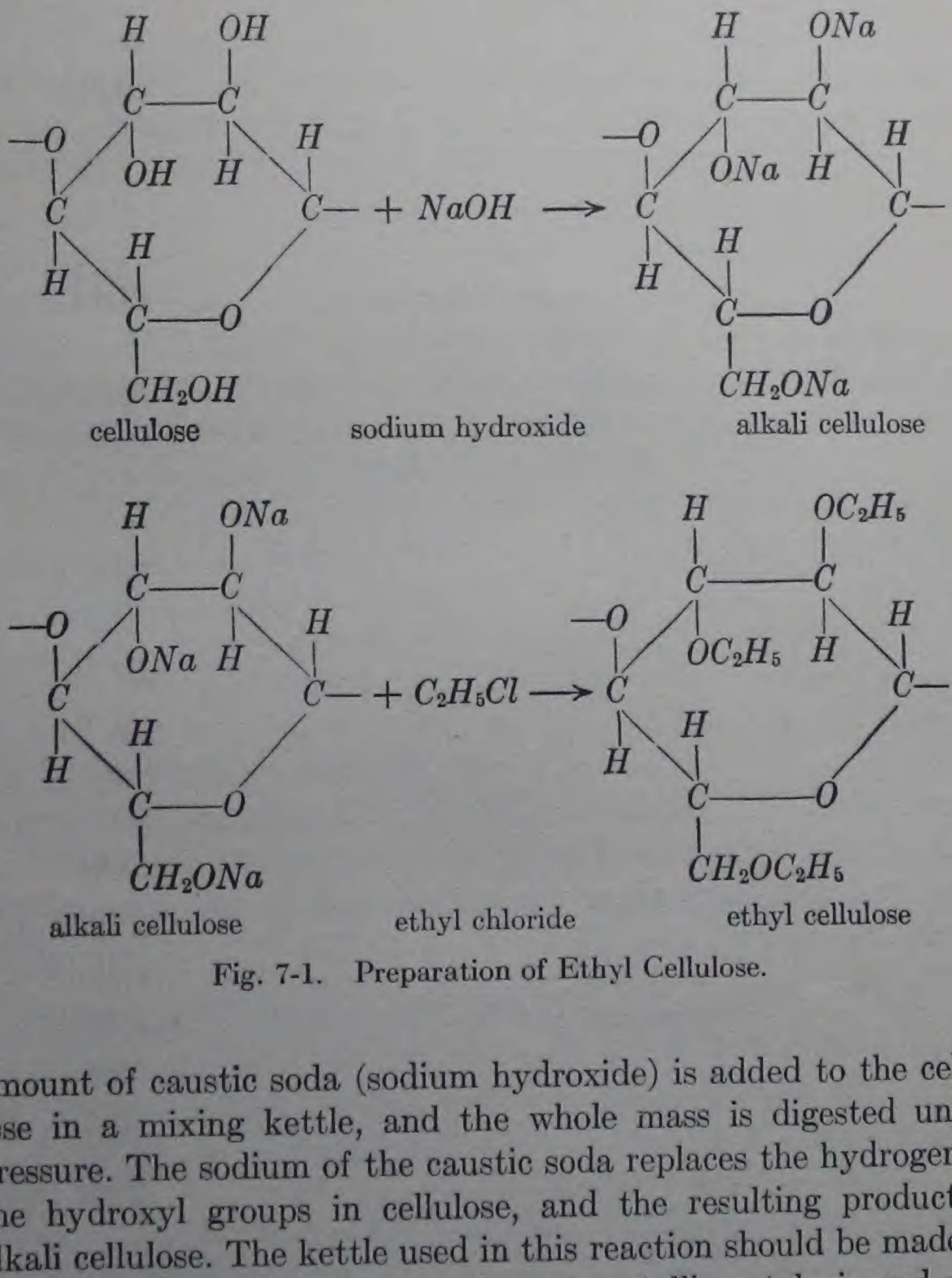


Fig. 7-1. Preparation of Ethyl Cellulose.

amount of caustic soda (sodium hydroxide) is added to the cellulose in a mixing kettle, and the whole mass is digested under pressure. The sodium of the caustic soda replaces the hydrogen of the hydroxyl groups in cellulose, and the resulting product is alkali cellulose. The kettle used in this reaction should be made of nickel or lined with nickel to prevent metallic catalysis and corrosion. At the conclusion of the reaction, the alkali cellulose is a thick syrupy liquid, and it is pumped from the storage tank to the reaction kettle. If the water were removed, the alkali cellulose would have the appearance of ordinary cellulose.

The treatment of alkali cellulose with ethyl chloride is best accomplished under pressure. The syrupy alkali cellulose is pumped into an autoclave, into which a stream of ethyl-chloride gas is allowed to flow. The temperature is controlled throughout this ethylating reaction. As in the case of the cellulose esters, the amount of chemical replacement will depend on the relative pro-

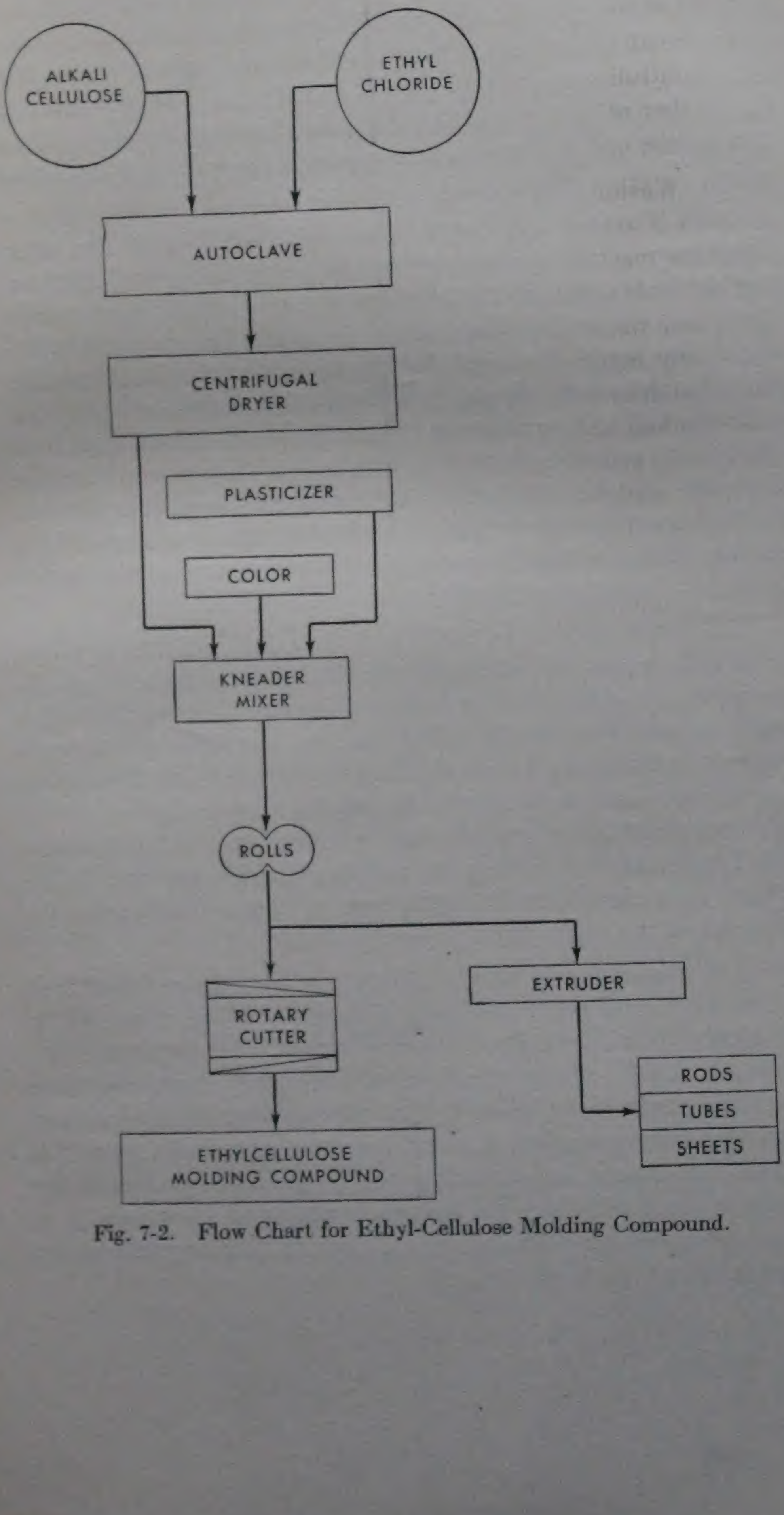


Fig. 7-2. Flow Chart for Ethyl-Cellulose Molding Compound.

portions of ingredients used and on the conditions under which the reaction takes place. In the case of the esters, the number of substitutions of the acetate or nitrate radical for the hydrogen of the hydroxyls can vary considerably. With ethyl cellulose, the reaction can be controlled more easily, since ethyl groups replace sodium. The number of hydrogen atoms replaced by sodium is well controlled in the original chemical reaction.

7-4. Washing and Drying Precipitate.—The next step after ethylating is to wash and dry the newly precipitated ethyl cellulose. During the reaction both ethyl ether and ethyl alcohol are formed. These solvents are recovered and are used in other chemical operations. Clear water is passed through the material several times to remove any excess solvent. The clean ethyl cellulose is put in a centrifugal drier to remove the water. Certain of the softer types of ethyl cellulose are suitable for molding as they come from the drier, but, in general, they do not possess good physical properties. The softer grades are used mainly for protective coatings, and for ethyl rubber. The harder grades of ethyl cellulose need plasticizers to render them suitable for injection or extrusion molding.

7-5. Manufacture of Molding Powder.—Plasticizer is incorporated by means of calendering or Banburying. Suitable plasticizers and dyestuffs are mechanically blended with the ethyl cellulose, and the mass is rolled until homogeneity is obtained. Polymerization is not involved in the formation of ethyl cellulose. The dense sheets have only to be put through rotary cutters to produce the molding powders. Some material is produced as rod and tube stock by running the molding powder through a continuous extruder. The size and shape of the die determine the diameter of the rod or tube.

7-6. Properties of Ethyl Cellulose.—It has been found that the properties of ethyl cellulose, exclusive of those imparted by plasticizers, are dependent on the extent of ethylation. For example, a 50% ethylation produces exceptional water resistance in the finished article; and a 45% ethylation produces an excellent low-temperature toughness. Ethyl cellulose is produced in several types, the properties depending on the base ethylation of the original alkali cellulose. Each type is produced in a variety of flows ranging from H_5 to S_5. The degree of flow depends on the amount and type of plasticizer.

Ethyl cellulose is compatible with a large number of waxes, resins, resin esters, and natural resins. It can be mixed with nitrocellulose in any desired proportions, but cannot be mixed at all with cellulose acetate or cellulose acetate-butyrate. Ethyl cellulose is an extremely soluble material, dissolving readily in most alcohols, ethers, ketones, and derivative compounds. Straight-chain hydrocarbons are about the only solvents that do not dissolve it. Ethyl cellulose is used extensively in the protective-coating field.

7-7. Ethyl Rubber.—Ethyl cellulose that is heavily plasticized with vegetable oils is called ethyl rubber. The material is flexible and exhibits some superior properties, such as resistance to ozone and mustard gas. This material may be injection molded, but thus far it has been made mostly into large cakes which can be sliced into thin sheets.

7-8. Formulation.—Ethyl cellulose needs no filler. It is a combination of binder and filler. Plasticizers used with it include such substances as castor oil, vegetable oil, phthalates, phosphates, and chlorinated hydrocarbons. No accelerators or retarders are needed.

A complete range of colors from crystal clear to black opaque is available in ethyl cellulose. Its clear transparent form is not so good as the acetate for light transmission. In general, the same types of coloring agents used with other cellulose derivatives may also be used with ethyl cellulose. The fact that ethyl cellulose is compatible with so many substances makes it possible to use additional coloring agents that sometimes cannot be used with other cellulose derivatives. A typical formula for an ethyl-cellulose molding compound is as follows:

	Per Cent
Binder and Filler (ethyl cellulose)	80
Plasticizer (cocoanut oil)	19
Color (spirit dye)	1

7-9. Other Cellulose Ethers.—Of the other cellulose ethers that have been marketed in the United States, the methyl and benzyl derivatives are the most important. These compounds have not been fully explored; so their potentialities are unknown. They are manufactured in the same way as ethyl cellulose but, instead

of using ethyl chloride to react with the alkali cellulose, a methyl or benzyl halide is used.

7-10. Applications.—The many diversified applications of ethyl cellulose are based on its good resistance to acids and alkalies, its dimensional stability, its good electrical properties, and its ability to blend (compatibility) with many other substances. When molded it is tough, stainproof, and resistant to chemicals. Ethyl cellulose can be molded by extrusion, compression, or injection into such articles as ice-cube trays, flashlight cases, aircraft control parts, substitute piping, and strips for decorative value on furniture.

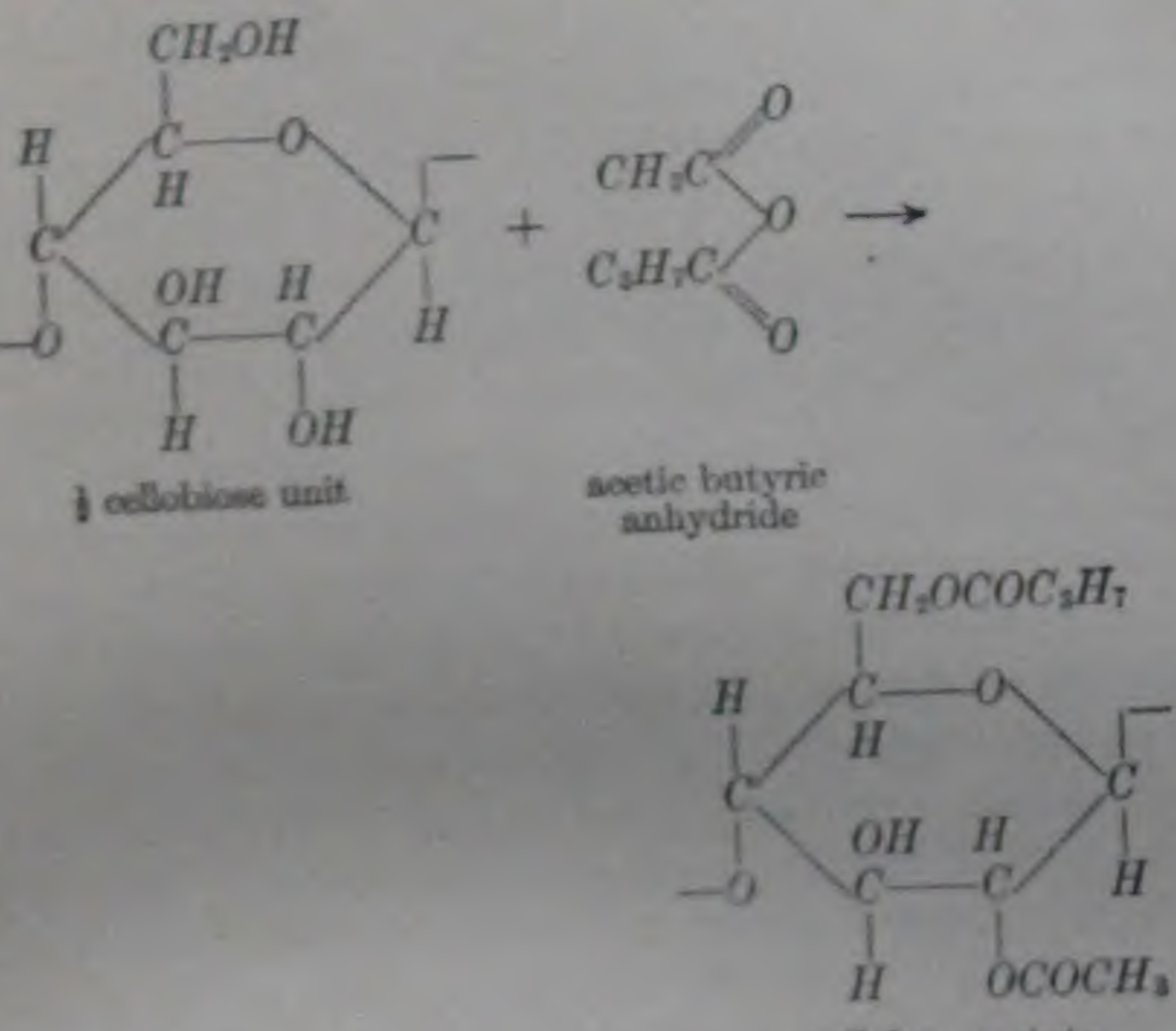
Ethyl-cellulose solution, either by itself or in modified form, is used for surface coatings, varnishes, and lacquers with a good extensibility because its film-forming qualities impart toughness, flexibility, and adhesiveness. Sheets, rods, and tubes of ethyl cellulose can be sawed, machined, and drawn. Some of the trade names are Ethocel, Ethofoil, Hercules Ethyl Cellulose, Lumarith E. C., and Nixon Ethyl Cellulose.

Cellulose Acetate-Butyrate

7-11. Chemistry.—Cellulose acetate-butyrate is classified as a thermoplastic material of the cellulose-derivative type. This material closely resembles cellulose acetate in physical properties, appearance, and adaptability. Certain differences between the two materials, however, require the use of one plastic where the other one would not be suitable.

The chemical reactions in the manufacture of butyrates are identical with those in the production of cellulose acetate; but, in addition to the materials used for making acetates, butyric acid and its anhydride are used. As the name indicates, cellulose acetate-butyrate is a mixed ester of cellulose. For ease in formula writing, the two anhydrides are thought of as a single mixed anhydride. The equation to represent the reaction in the preparation of cellulose acetate-butyrate is as shown in Fig. 7-3.

7-12. Raw Materials.—Most of the raw materials used in the production of the butyrates are the same as those used for the acetates. The butyric anhydride is prepared directly from butyric acid, which, in turn, is made by several processes. This acid can be



1 cellobiose unit

acetic butyric anhydride

cellulose acetate butyrate

Fig. 7-3. Preparation of Cellulose Acetate-Butyrate.

derived from butyl alcohol by direct oxidation or by the fermentation of the lactic acid present in sour milk. Decaying cheese, which contains butyric "ferment," and chalk are added to sour milk. The chalk is added to act as a neutralizer, because the ferment will not start the reaction if the solution is too acid.

7-13. Method of Manufacture.—Cellulose acetate-butyrate is made by the processes and operations used for cellulose acetate. The acetate-butyrate is not marketed in so many formulations as the acetates, because of its versatility. That is, an acetate needs two or three formulas to possess the good qualities that an acetate-butyrate possesses in one formulation. The material is produced in a variety of flows, insuring proper movement under heat and pressure for almost any application.

7-14. Comparison of Acetates and Acetate-Butyrates.—The fact that acetate-butyrates are mixed esters means that the proportions of the various anhydrides can be changed. Since the process of manufacture is identical for acetates and acetate-butyrates, the fact that acetate-butyrates have some definite

advantages in physical and chemical properties over acetates can be explained only by the presence of a mixed ester. In acetate, an acetate group is always substituted for a hydrogen atom. With acetate-butyrate, the substitution is sometimes a butyrate radical for a hydrogen atom, and sometimes an acetate radical for a hydrogen atom. By changing the proportions of the anhydride mix, many interesting properties can be obtained.

The total effective substitution is the same for both acetate and butyrate. Furthermore, the substitution is haphazard. To produce good, uniform molding powders, the cellulose structure should be substituted in a conjugated manner. For example, suppose a cellulose chain contains 100 glucosidic groups, each of which contains three replaceable hydroxyl groups. Suppose, further, that 30 of these hydroxyls were to be replaced by acetate or butyrate radicals. The 30 hydroxyls to be replaced should be scattered throughout the whole chain and should not be confined to only a small portion of it. If replacement takes place in only a portion of the chain, the compound will be top-heavy, and a non-uniform molding material will result. The best method of maintaining a good, uniform chain is by rigidly controlling the reaction temperature, the time, and the proportions of the ingredients.

Cellulose acetate of high acetyl content approaches the physical and chemical properties of the acetate-butyrates. The high-acetyl compounds are much harder than the acetate-butyrates; so, in order to equal the ease of flow of the acetate-butyrates, they must be plasticized rather heavily. Acetate-butyrates possess the pungent, disagreeable odor of butyric acid. In recent years, deodorants have been added, but they have not proved entirely satisfactory. Another method of getting rid of the odor is by dipping the molded article in a warm, mild soap solution. This dipping has the effect of neutralizing the surface acid and dispelling the odor. High-acetyl acetates do not have an odor, and, in this respect, they have an advantage over the acetate-butyrates.

7-15. Formulation of Butyrate Plastics.—Cellulose acetate-butyrate, often called acetobutyrate, acts as both binder and filler. In formulating, the plasticizers are the ones that are used with acetate compounds and also some that cannot be used with the acetates. The butyric acid acts somewhat as an integral plasticizer; thus, the required amount of auxiliary plasticizer is reduced.

Since butyrate does not undergo polymerization, no accelerator or retarder need be used. Acetobutyrates are available in a wide range of colors. The clear transparent is not so good as the related acetate material. Almost any dyestuff or pigment can be used as the coloring agent.

The composition of a typical molding compound is as follows:

	Per Cent
Binder and Filler (cellulose acetate-butyrate)	79
Plasticizer (dimethyl phthalate)	20
Color (dyestuff)	1

Work has been done with other mixed esters, but so far the acetate-butyrate ester is the only one that is satisfactory as a molding compound. Cellulose acetate-propionate yields a good lacquer-base material rather than a molding compound. In the propionate, propionic acid and anhydride replace about two-thirds of the acetic acid and anhydride.

7-16. **Applications.**—Cellulose-acetate-butyrate molding compounds are suited to uses where resistance to distortion by heat, humidity, and weathering are desired. Although the material may be injection molded or compression molded, a considerable amount of material is being produced in extruded forms, such as strips, rods, tubes, and special shapes. These forms are used as substitutes for metal and wood in weather stripping, structural moldings, edgings, and wallboard trim. Woven strips have been applied to chair seats and furniture, and to apparel items such as ladies' handbags, millinery, and shoes.

Considerable success in molding large pieces with cellulose acetate-butyrate has been reported. Cellulose acetate-butyrate is being extensively investigated because of its ability to endure abuse in handling and because of its stability under all climatic conditions. Housings for business machines, gunstocks, army bugles with clarity and tonal quality surpassing those of the brass instrument, and tooth-brush handles are being molded of cellulose acetate-butyrate in increasing numbers. Textile yarns, varnishes, adhesives, and coating solutions make up other outlets for the material. Tenite II is a trade name for manufactured cellulose acetate-butyrate.

Vinyl-Ester Resins

7-17. Types of Vinyl-Ester Resins.—Vinyl chloride and vinyl acetate are vinyl-ester resins, and both are classified as thermoplastic materials of the synthetic resin type. Both contain basically the vinyl structure; therefore, they belong to the vinyl-resin family.

7-18. Vinyl Acetate.—Vinyl acetate is a water-clear liquid that boils at 73° C when in its monomeric state. Structurally, as its name indicates, it is a combination of a vinyl grouping and an acetate grouping, or $CH_2{=}CHOCOCH_3$. Like styrene, another member of the vinyl family, vinyl acetate can polymerize to form resins. The resin structure for polymerized vinyl acetate is a straight-chain arrangement like that shown in Fig. 7-4.

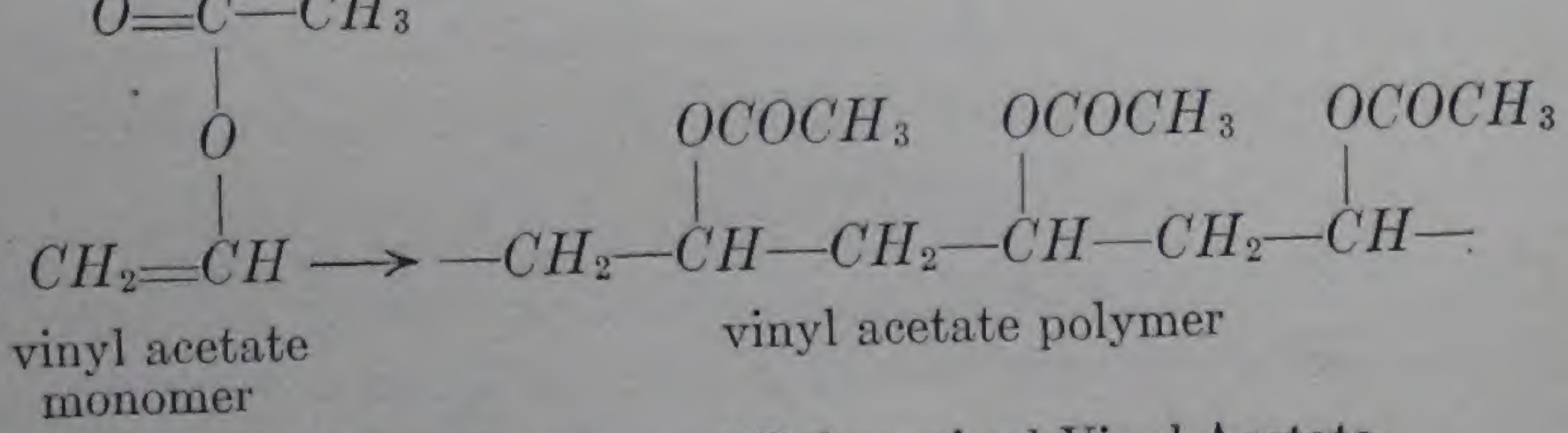
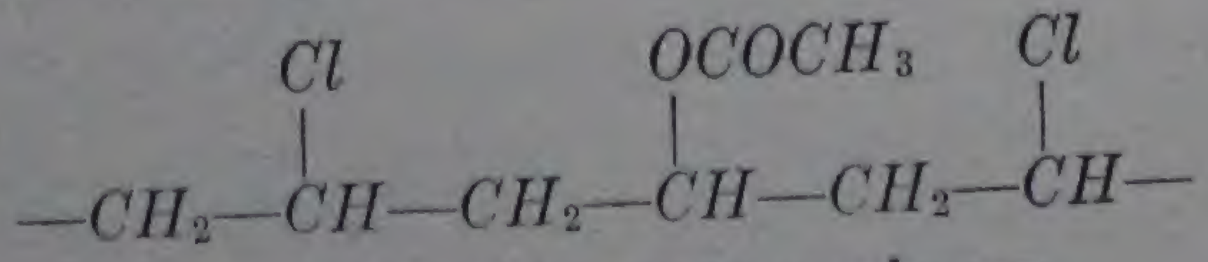


Fig. 7-4. Structure of Polymerized Vinyl Acetate.

7-19. Vinyl Chloride.—Vinyl chloride is simply vinyl acetate with the $OCOCH_3$ group replaced by a chlorine atom. Normally a gas at room temperature, it can be made to polymerize alone or in conjunction with other vinyl-ester monomers, provided the conditions for polymerization are controlled. If vinyl acetate and vinyl chloride polymerize together, they form a resinous product whose structure is shown in the following formula:



Satisfactory resins are produced with the aid of suitable catalysts and the correct proportion of acetate and chloride. The ratio of the number of acetate ($OCOCH_3$) radicals to the number of chlorine atoms in the polymer chain varies; furthermore, their positions in the chain may not be alternating, but it is

possible that they occupy other positions as well. This process of polymerizing two or more substances together is called copolymerization and the product is called a copolymer. The copolymer of vinyl acetate and vinyl chloride possesses superior properties.

7-20. Raw Materials.—There are abundant raw materials from which vinyl esters can be synthesized. Acetylene, which is a basic ingredient of both vinyl acetate and vinyl chloride, is made from calcium carbide; and this substance is made from coal and limestone. The reaction of acetylene with acetic acid forms vinyl acetate, whereas that with hydrochloric acid forms vinyl chloride. Proper precautions, including choice, preparation, and purity of catalyst and time and temperature of the reaction, must be taken to prevent undesirable side reactions from occurring when acetylene is one of the reactants. The reactions for the preparation of vinyl chloride and vinyl acetate are shown in Fig. 7-5.

$$HC{\equiv}CH + HCl \xrightarrow[\text{heat}]{\text{catalyst}} CH_2{=}CHCl$$

vinyl chloride

$$HC{\equiv}CH + CH_3COOH \xrightarrow{\text{catalyst}} CH_2{=}CH{-}O{-}C(=O){-}CH_3$$

vinyl acetate

Fig. 7-5. Preparation of Vinyl Chloride and Vinyl Acetate.

7-21. Molding Compounds.—In the production of the vinyls, the equipment should be of aluminum, glass, or stainless steel. In the case of vinyl chloride, the chlorine atom is not stable and it will form hydrochloric acid under adverse conditions. If any iron is present, a chemical reaction will take place which will ruin both the resin and the equipment.

Vinyl-acetate polymerization is done in an autoclave in the absence of air. A catalyst such as benzoyl peroxide will aid the reaction, as will ultra-violet light. The polymerization should proceed slowly and uniformly, and in order to start polymerization a small amount of heat is added. Since the amount of heat and the amount of catalyst used have a decided effect on the rate of polymerization, they must be controlled. When the correct molecular weight is reached, the reaction is stopped by removing the heat and introducing an inhibitor such as sulfur. The polymer is care-

fully dried, and the clear white solid that results is ground and stored for further use.

The polymerized form of vinyl acetate is called polyvinyl acetate. It finds its main use as an adhesive for leather scrap and paper. Polyvinyl acetate is compatible with a great many solvents, resins, and plasticizers. The product is made in several degrees of viscosity, depending on the use for which it is manufactured.

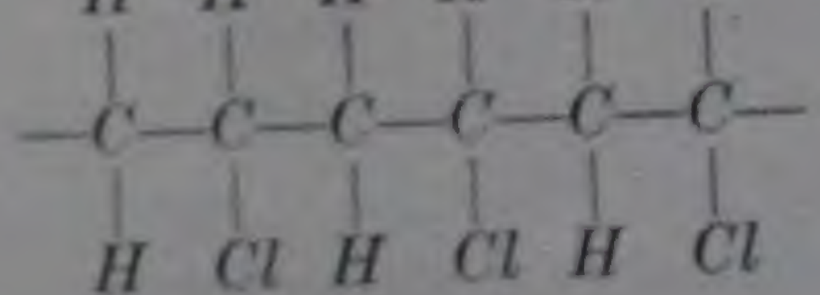
The polymerization of vinyl chloride in the gaseous state is slow, but it can be rapid if the gas is liquefied at reduced temperatures. Ultra-violet light or benzoyl peroxide is used as an accelerating catalyst. When the proper degree of polymerization has been reached, the reaction is stopped by removing the heating medium. The resin, polyvinyl chloride, is dried and pulverized. It is used as a molding compound but it must be plasticized. Since compounds of this type tend to decompose on high heating to form hydrochloric acid, lead salts are incorporated with the plasticizer to prevent this decomposition.

7-22. **Copolymer of Vinyl Chloride and Acetate.**—Both polyvinyl acetate and polyvinyl chloride possess some excellent qualities. A copolymer of the acetate and the chloride combines the best properties of each. Copolymerization is accomplished by mixing monomeric vinyl chloride and monomeric vinyl acetate with a solvent, the reaction being accelerated by a catalyst. An autoclave is used, as with the individual materials. Thousands of copolymers are theoretically possible by simply varying the ratio of chloride to acetate. Common mixes contain from 80 to 95 per cent of chloride and from 20 to 5 per cent of acetate. Special copolymers can be made for specific applications. The higher the molecular weight, the tougher and more soluble the compound. The copolymer is also called polyvinyl chloracetate.

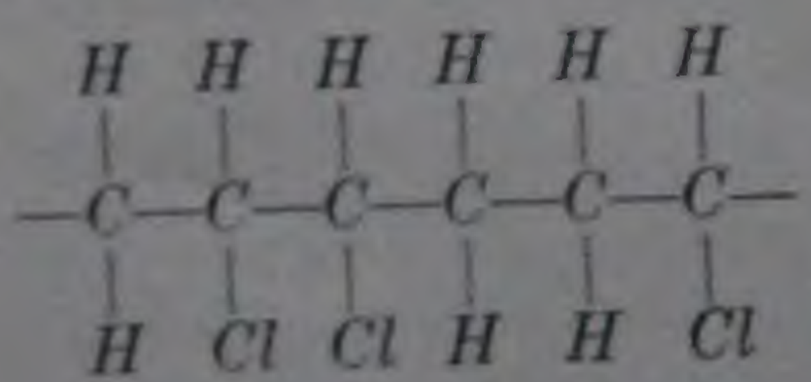
Copolymers are supplied in both filled and unfilled compounds. They are also produced as either flexible or rigid molding compounds. An unplasticized, unfilled compound is rigid and is almost unmoldable. Small amounts of plasticizer bring the compound down in the molding range, and large amounts of plasticizer reduce the compound to a flexible state. The incorporation of small amounts of filler, such as mica or silica, in a heavily plasticized material presents certain advantages in the physical properties.

Copolymers are further compounded by a rolling or Banburying process. Plasticizer, filler, lubricant, and coloring matter are all premixed with the powdered polymer. The entire mix is finely dispersed in a solvent to make the rolling process easier. Then the excess solvent is evaporated, leaving a putty-like mass that is fed to the rolls. In the rolling operation, all the ingredients are thoroughly kneaded together into a uniform mix. The material is cut away from the rolls and is granulated by rotary cutters. Since these materials are thermoplastic, there is no chemical change during the rolling operation. The change is purely physical. The copolymer may be extruded to form sheets, rods, and tubes, or it may be formed into a block to be sliced into sheets. Several formulations and degrees of flow are manufactured with a complete color range from water-white transparent to black opaque.

7-23. Methods of Copolymerization.—When straight-chain hydrocarbons polymerize, there is always a straight succession of carbons and hydrogens in the chain. When a substitute hydrocarbon like vinyl chloride polymerizes, there are apparently three ways in which the molecules can join to form the polymer. If the molecules combine to form a regular chain that has a substituted group on every other carbon atom, it is known as "head-to-tail" polymerization. This arrangement of vinyl-chloride molecules is represented as follows:

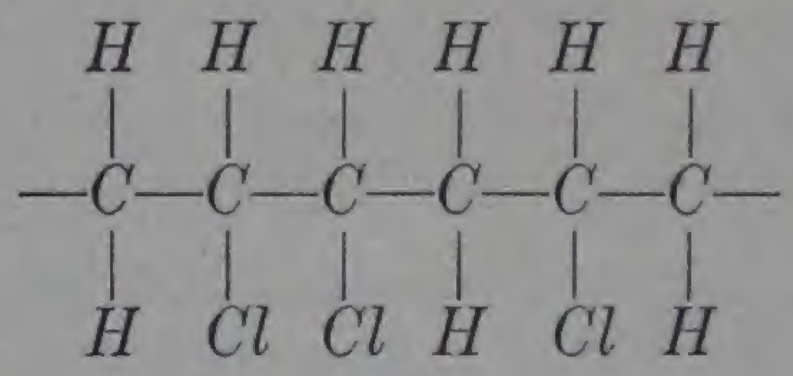


If the combination forms so that the substituted groups occur in pairs, it is called "head-to-head" polymerization. This arrangement of vinyl-chloride molecules is represented as follows:



The molecular weights of both compounds are identical, and the per cent of chlorine is the same.

A chain of both head-to-head and head-to-tail polymers is theoretically possible, with the following constitutional formula:



Investigators in this field have been unable to definitely identify polymers of this type; therefore the existence of such polymers has not been fully proved. It is generally accepted that the head-to-head polymerization is the one most likely to occur.

7-24. General Discussion.—Vinyl-ester resins are used in many different fields. At the present time, their use as a molding powder constitutes about the smallest use of the material. They are more often used as adhesives and as impregnating resins for waterproofing and fireproofing. When used as molding materials, the vinyl-ester resins must be plasticized. A variety of plasticizing materials are available, the most common being dioctyl phthalate and tricresyl phosphate. The plasticizer content will vary from 10 to 60 per cent, the amount depending on the degree of rigidity or flexibility desired. The vinyl-ester resins are easily colored by various dyes and inert pigments. These resins are self-lubricating. Since they are permanently thermoplastic, no accelerator or retarder is used.

If the vinyl ester is used as an adhesive or a coating, the choice of solvents used for solution is important. Vinyl chloride is soluble in cyclohexanone and nitrobenzene. Since both of these are far too slow in drying to be used in coating formulations, the solution is usually adulterated with nitroparaffins and ketones to insure fast surface drying. Vinyl acetate differs from the chloride in being soluble in a wide variety of commercial solvents. The copolymers have a solubility range between the two individual materials.

7-25. Applications of Polyvinyl Chloride.—Polyvinyl chloride is available as granular powder, plasticized sheets, solutions of the plasticized resins, extruded tubing, and special shapes. Flexible articles may be produced by compression molding, but the demand for such products is not great. Larger volumes of the resin go into the making of extruded tubing and hose and into the coating of

wire cables by extrusion. Such coatings provide better electrical insulation and waterproofness than the materials, such as varnished cambric, formerly used for these functions. Sheet stock is being used to line tanks containing corrosive chemicals. Besides being chemically inert, the sheet retains its flexibility much longer than rubber, and it does not crack so easily on exposure to sunlight. Solutions of polyvinyl-chloride resin are used effectively to impregnate fabrics for waterproofness and in imitating real leather. Koroseal, Koron, Flamenol, and Korogel are trade names of certain manufacturers' products.

7-26. Applications of Polyvinyl Acetate.—Some of the properties exhibited by polyvinyl chloride are found in polyvinyl acetate, and in addition the acetate compound is soluble in many organic solvents and is compatible with other materials. Leather lacquer finishes, adhesives for glass, cloth, paper, metal, wood, and porcelain, and printing inks bear out these properties.

Good adhesion is accomplished by one of several methods. The solid resin can be applied as a hot melt, as a solution in organic solvents, or as a water emulsion. Its lack of taste, odor, and color, in addition to its bonding characteristics, make the material ideally suitable as an adhesive for drinking cups and food containers. The filled compound can be used for molding purposes under pressure and as a plastic wood. However, the compound is not extruded nor molded, as it tends to stick to the mold surfaces. The resin is usually filled with wood flour and is dissolved in a solvent to make the preparation known as plastic wood. The preparation is applied to cracks or holes in wood, and is used similarly to clay in modeling. The application shrinks very little after the solvent has evaporated, and it is extremely hard. Furthermore, it can be nailed, sawed, and drilled with no harmful effects.

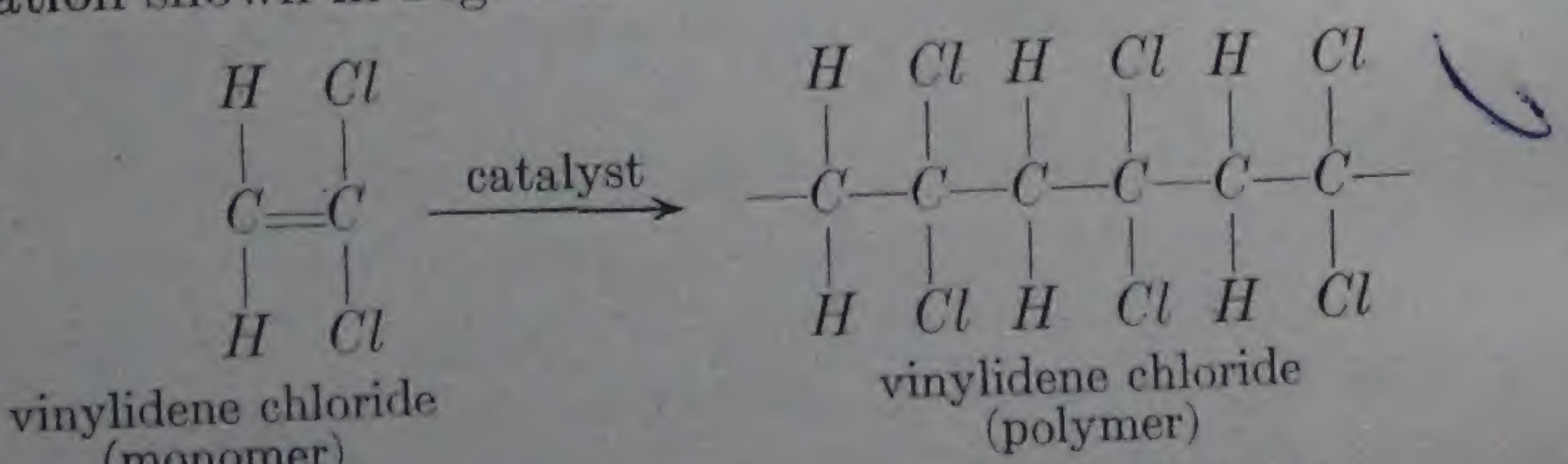
7-27. Applications of Polyvinyl Chloride-Acetate.—The best properties of the individual vinyl chloride and vinyl acetate exist in combination in the copolymer of the two esters. The compound is fabricated into rods, sheets, tubes, film foil, molding compounds, protective coating solutions, and fibers or minute strands as substitutes for conventional yarns. It is odorless, tasteless, nontoxic, non-flammable, non-warping, non-shrinking, and tough. It has excellent water and chemical resistance and good electrical

properties. Articles that have been made of polyvinyl chloride-acetate include waterproof shower curtains, transparent belts, suspenders, and wrist-watch bands; the synthetic fiber, Vinyon; rattan substitutes in chair seats; women's shoes and other apparel items; and lining for food containers and beverage cans. Products are marketed under the trade names of Vinylite and Vinyon.

Vinylidene Chloride

7-28. Chemistry.—Vinylidene chloride, like vinyl acetate and vinyl chloride, is an aliphatic compound that contains the vinyl group. Resistance to chemicals and solvents and low water absorption are some of the outstanding properties that make it a superior plastic. Polymers of vinylidene chloride are thermoplastic and are made from common substances.

Vinylidene chloride, or unsymmetrical dichloroethylene, is easily prepared from ethylene, which is a gas derived from petroleum cracking, and chlorine, which can be obtained from the electrolysis of brine. It is a clear, colorless liquid that boils at 31.7° C and has the structural formula $CH_2{=}CCl_2$. The formula shows the chlorine atoms attached to the same carbon atom; hence, the compound is unsymmetrical. Under proper conditions of catalyst and temperature, vinylidene chloride polymerizes according to the equation shown in Fig. 7-6.



vinylidene chloride (monomer)

vinylidene chloride (polymer)

Fig. 7-6. Polymerization of Vinylidene Chloride.

7-29. Manufacture of Vinylidene-Chloride Polymer.—In the manufacture of vinylidene-chloride polymer, ethylene and chlorine are brought together to produce trichloroethane, $CH_2Cl{\cdot}CHCl_2$. Lime is then reacted with this compound to remove a molecule of hydrogen chloride to produce vinylidene chloride, $CH_2{=}CCl_2$. The equations to represent these reactions are shown in Fig. 7-7.

A flow chart for the production of vinylidene chloride is shown in Fig. 7-8. Special equipment must be used to withstand

Fig. 7-7. Preparation of Vinylidene Chloride.

the corrosive action of the reactants and of the products of the reaction. The monomer must be completely separated from the other reaction products that may contaminate it, such as hydrogen chloride and excess lime, before it can be polymerized.

The polymerization of vinylidene chloride is appreciably aided by the addition of a catalyst such as benzoyl peroxide or lead tetraethyl. After the catalyst has been added, heat is applied rather slowly. The rate of temperature rise controls the length of the polymer chain as indicated by viscosity measurements. When the proper degree of viscosity has been reached, the heat is turned off and the material is allowed to cool. The polymerization is a slow process, sometimes taking several days. Handling in later stages is facilitated by pouring the polyvinylidene chloride into shallow trays to stabilize its temperature. The polymer is ground to a powder preparatory to mixing.

The ground resin is mixed with dyes and plasticizers on a calender roll or in a Banbury mixer. The resultant milled compound can be ground and used in injection molding, or it can be fed directly to an extruder for the production of filaments.

7-30. Physical Structure and Properties.—Although most organic thermoplastics exist in an amorphous state and do not exhibit crystallinity, X-ray studies have proved that the polymer of vinylidene chloride possesses a crystalline structure. This is strikingly different from any plastic so far discussed. Until a method of orienting the crystals was discovered, they were arranged in a haphazard manner. Orienting the crystals is accomplished by a simple stretching operation under slow cooling. A section of polyvinylidene-chloride resin, part of which has been stretched to orient the crystals, is shown graphically in Fig. 7-9. Orientation by stretching is a well-known process in the synthetic-fiber industry. The physical properties of an oriented material are far superior to those of an unoriented material. The tensile strength,

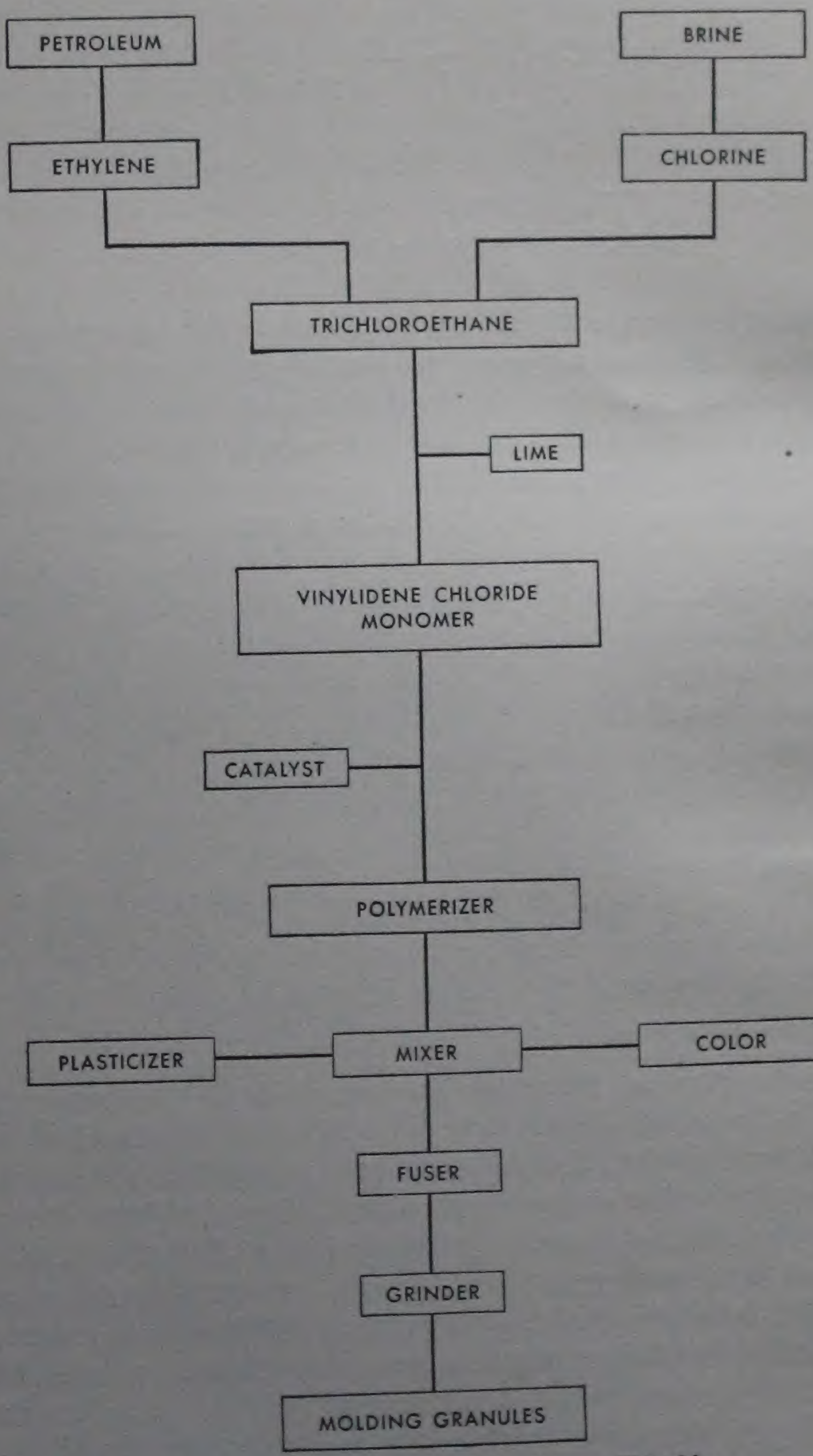


Fig. 7-8. Flow Chart for Vinylidene Chloride.

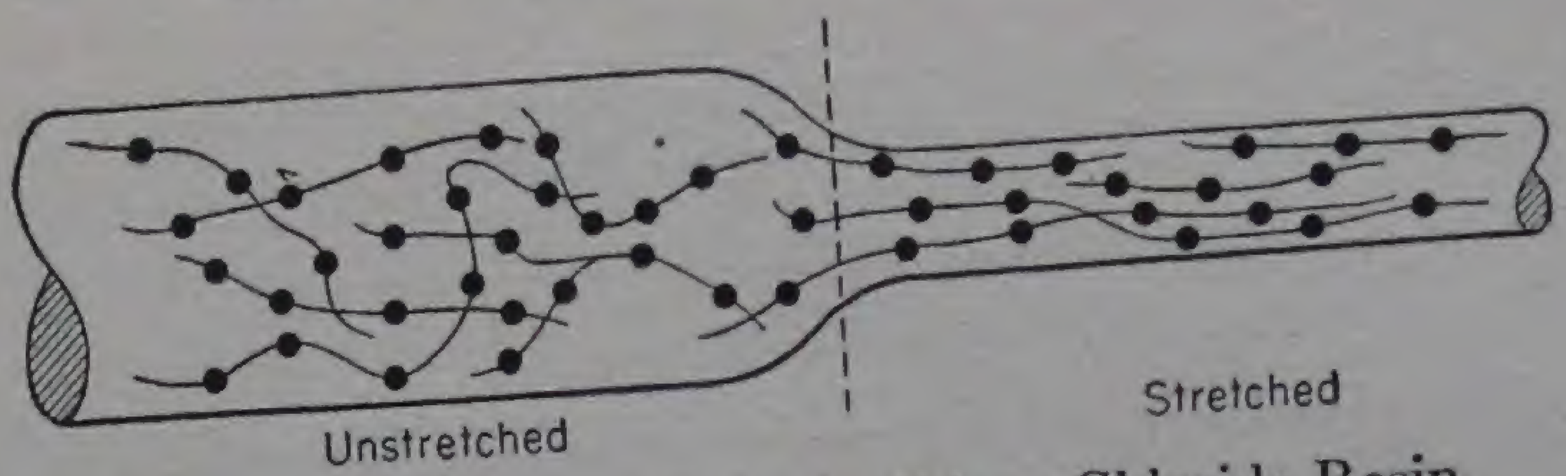


Fig. 7-9. Section of Polyvinylidene-Chloride Resin.

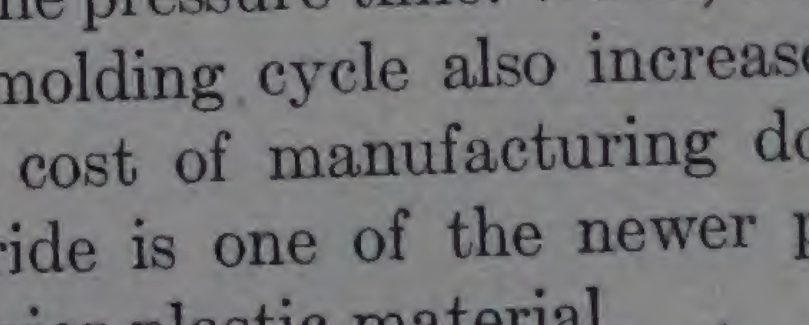
for example, can be increased about fivefold by orientation. The flexural strength of an oriented material is infinitely greater than that of the unoriented material.

An amorphous polymer can be made under special conditions, and it can then be crystallized either by heat treatment or by mechanical working. The amorphous plastic is somewhat flexible, whereas the crystalline form attains maximum rigidity and toughness at the sacrifice of flexibility.

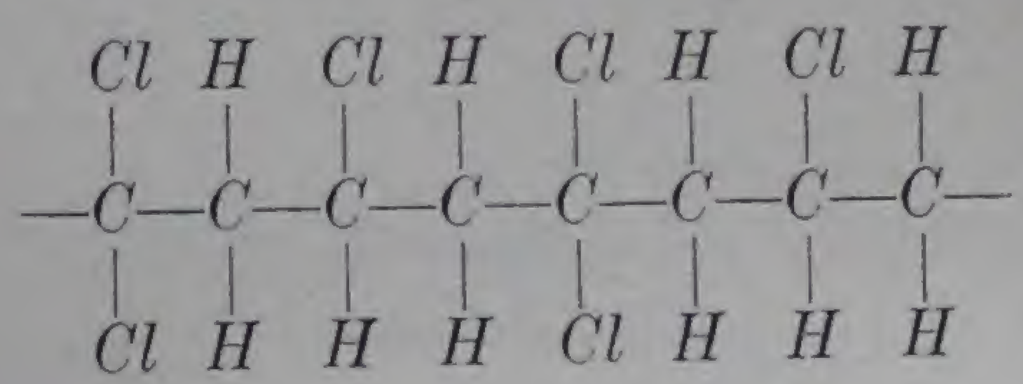
Polyvinylidene chloride is very sensitive to heat. The chlorine molecule, as pointed out in the discussion of polyvinyl chloride, is not fixed, and extreme temperatures cause the formation of hydrochloric acid which causes serious corrosion problems. This condition has made it necessary to use special metals wherever there is contact with hot polyvinylidene chloride. Also, iron and copper-base metals catalytically aid the thermal decomposition of the resin in hot zones above 130° C.

Polyvinylidene chloride cools faster than any other thermoplastic material, owing mainly to recrystallization. The value of this rapid cooling can be fully appreciated by once more analyzing the meaning of pressure time. The slower the cooling rate of a material, the longer the pressure time. When, however, the pressure time increases, the molding cycle also increases. As the molding cycle increases, the cost of manufacturing does likewise. While polyvinylidene chloride is one of the newer plastics, it is being recognized as a superior plastic material.

X-ray analysis not only has shown that the polymer is crystalline in structure, but also has indicated the manner in which the single molecules are linked to form the larger molecules, or polymers. Evidence points to a head-to-tail chain, as follows:



7-31. Copolymerization.—Vinylidene chloride can be copolymerized with almost all of the other vinyl compounds. The structure of a copolymer depends entirely on the ratio of materials used and on the polymerizing conditions. In copolymerizing vinylidene chloride, the emulsion method is often preferred. A typical one-to-one copolymer of vinylidene chloride and vinyl chloride is shown in the following structural formula:

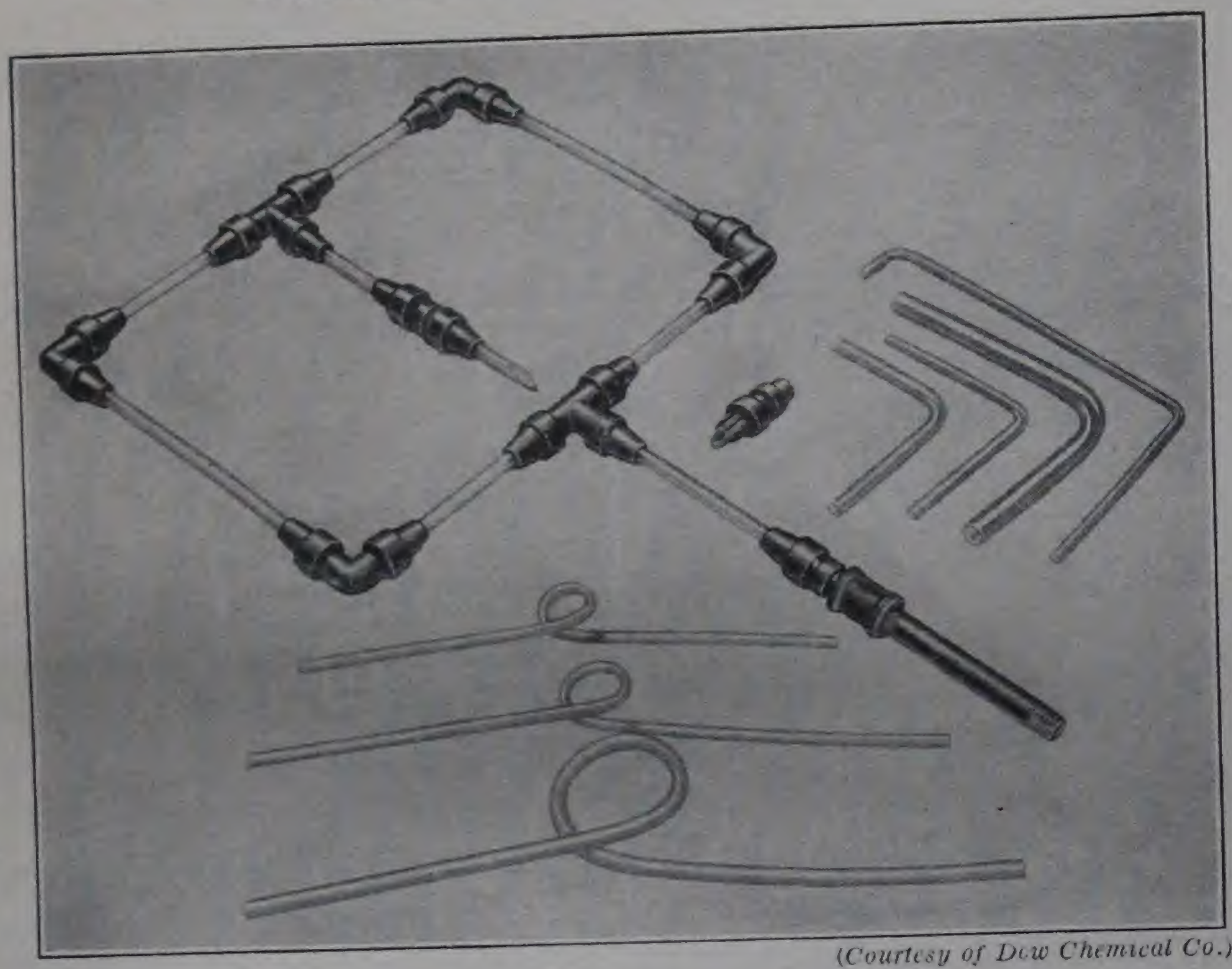


Copolymers produce a variety of materials with an equal variety of properties.

7-32. Formulas and Applications.—Polyvinylidene chloride can be produced in a molding composition that imparts flexibility to the molded article. Many different substances are compatible with the polymer and are used as plasticizers. Some of the more common ones are the aromatic chlorine derivatives such as dichlorobenzene and chloronaphthalene. The amount of plasticizer used determines the flexibility. Rigidity and greater strength are properties of other molding compositions which are obtainable as specified.

No lubricants or accelerators are used in the manufacture of polyvinylidene chloride. Inhibitors such as pyridine are sometimes used to prevent polymerization if the monomer is to be stored for any length of time. The inhibitor is removed before polymerization by distillation or alkali extraction. Since the resin has a high degree of strength and the addition of filler would tend to impair this property rather than aid it, the molding compound is usually supplied without filler. Polyvinylidene chlorides are available in a wide range of colors. Satisfactory colorings are obtained from vat and naphthol dyes or from organic pigments. The composition of a typical vinylidene-chloride molding compound is as follows:

	Per Cent
Binder (vinylidene chloride)	70
Plasticizer (1, 3-chlorobenzene)	28
Color (titanium dioxide)	2



(*Courtesy of Dow Chemical Co.*)

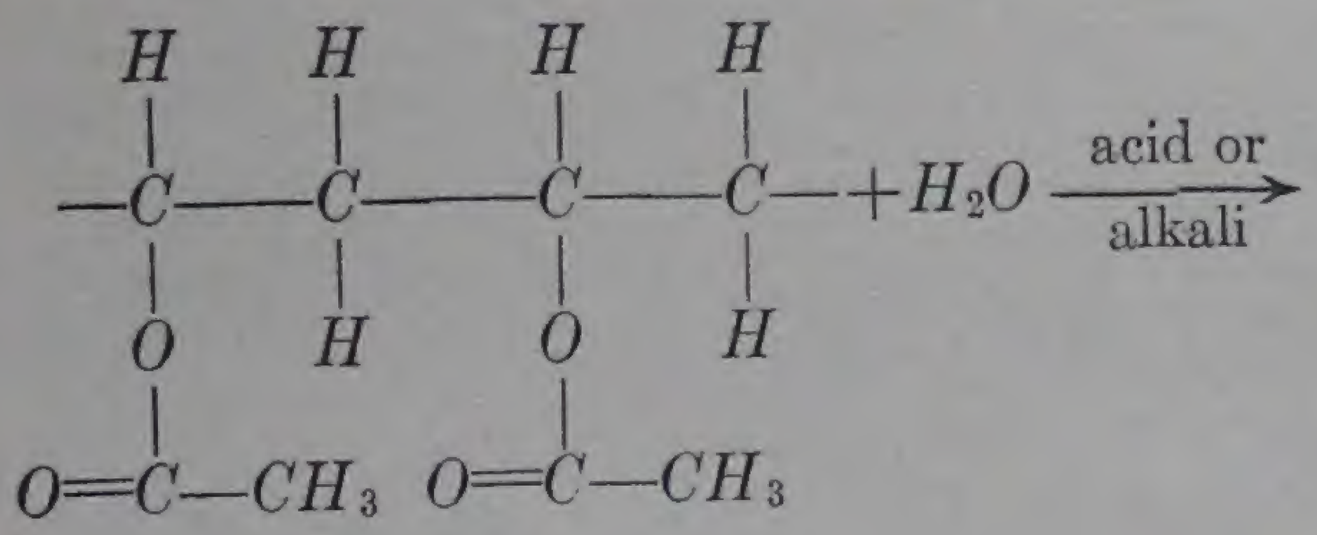
Fig. 7-10. Saran Tubing and Fittings.

Polyvinylidene chloride can be obtained as a granular molding powder; in the form of a film or foil; as sheets, rods, or tubes; as extruded shapes; as fibers; or as a solution for coating purposes. The polymer can be extruded, drawn, formed, molded by either injection or compression, and machined.

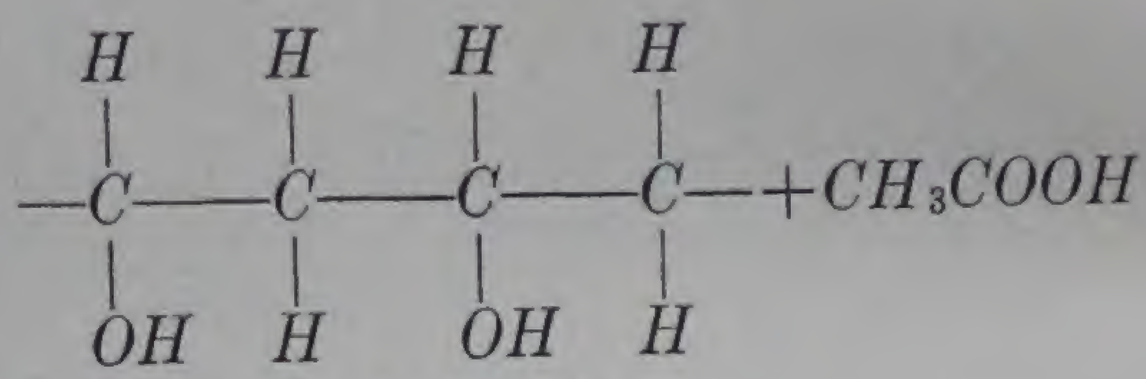
Such articles as furniture webbing, screening, wire coatings, belts and suspenders, watch straps, chemical tubing or piping, and spray-gun parts are made of polyvinylidene-chloride resins. The tubing and fittings shown in Fig. 7-10 are manufactured from polyvinylidene chloride that appears on the market under the name of Saran, which is the trade name coined by the manufacturer.

Polyvinyl Alcohol and Polyvinyl Acetals

7-33. Polyvinyl Alcohol.—Polyvinyl alcohol is obtained when polyvinyl acetate undergoes hydrolysis. The reaction is carried out in the presence of a catalytic agent, usually an acid or alkali, and the transformation is represented by the equation indicated in Fig. 7-11.



polyvinyl acetate



polyvinyl alcohol

Fig. 7-11. Production of Polyvinyl Alcohol.

Polyvinyl alcohol may be modified with plasticizing agents to form rubber-like plastic compounds. In general, it is made into grease-resistant and oil-resistant foils. The polymer is an intermediate step in the production of the more important vinyl-acetal compounds. Polyvinyl acetate may be hydrolyzed to any extent, the proper degree depending on the properties desired in the polyvinyl-alcohol finished product. The completely hydrolyzed compound is used for foils and packaging. Owing to its solubility in water, the partially hydrolyzed compound is made into adhesives and emulsions that are removable by merely moistening the dried application.

7-34. Polyvinyl Acetals.—Polyvinyl acetals are formulated from vinyl acetate. The preparation consists in first obtaining a polymer of vinyl acetate and then dissolving the polymer to prepare it for the subsequent transformation. The polymerization reaction of vinyl acetate takes place as shown in Fig. 7-4 on page 160. Polyvinyl alcohol is formed by the addition of a suitable reagent, sometimes acid but usually alkali, to the polyvinyl acetate. In the reaction the $OCOCH_3$ groups are replaced by the hydroxyl groups (OH). The final step in the production of polyvinyl acetal involves the addition of an aldehyde to form a polyvinyl acetal compound as a condensation product. The condensation reaction of butyraldehyde with polyvinyl alcohol, which is given for illustrative purposes, is shown in Fig. 7-12.

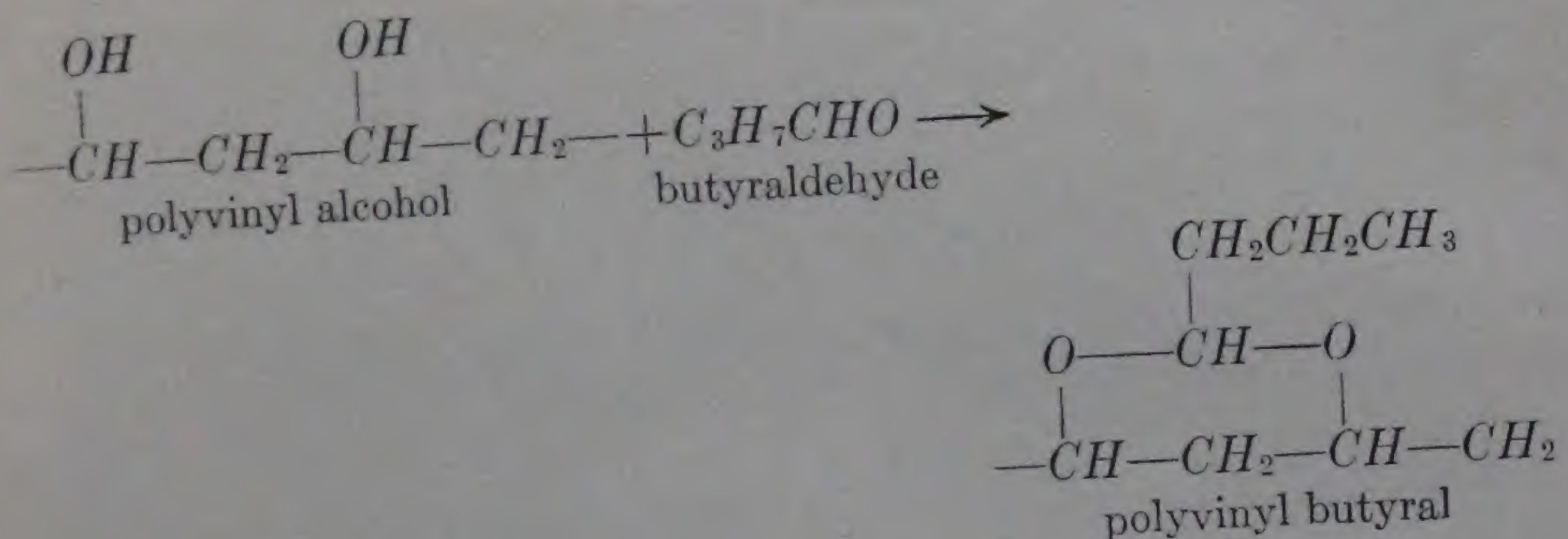


Fig. 7-12. Preparation of Polyvinyl Butyral.

The corresponding condensation products with formaldehyde and acetaldehyde are as shown in Fig. 7-13.

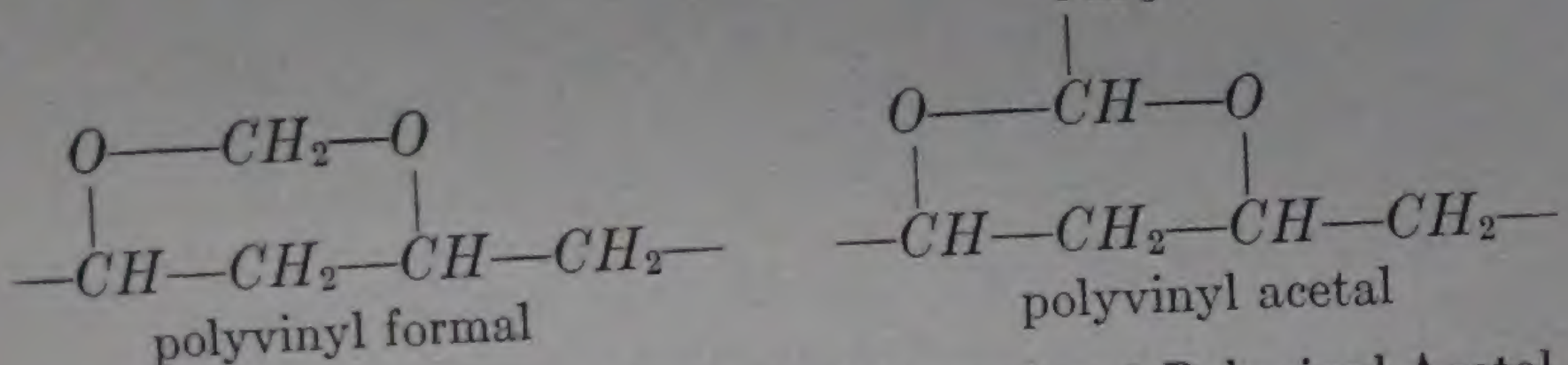
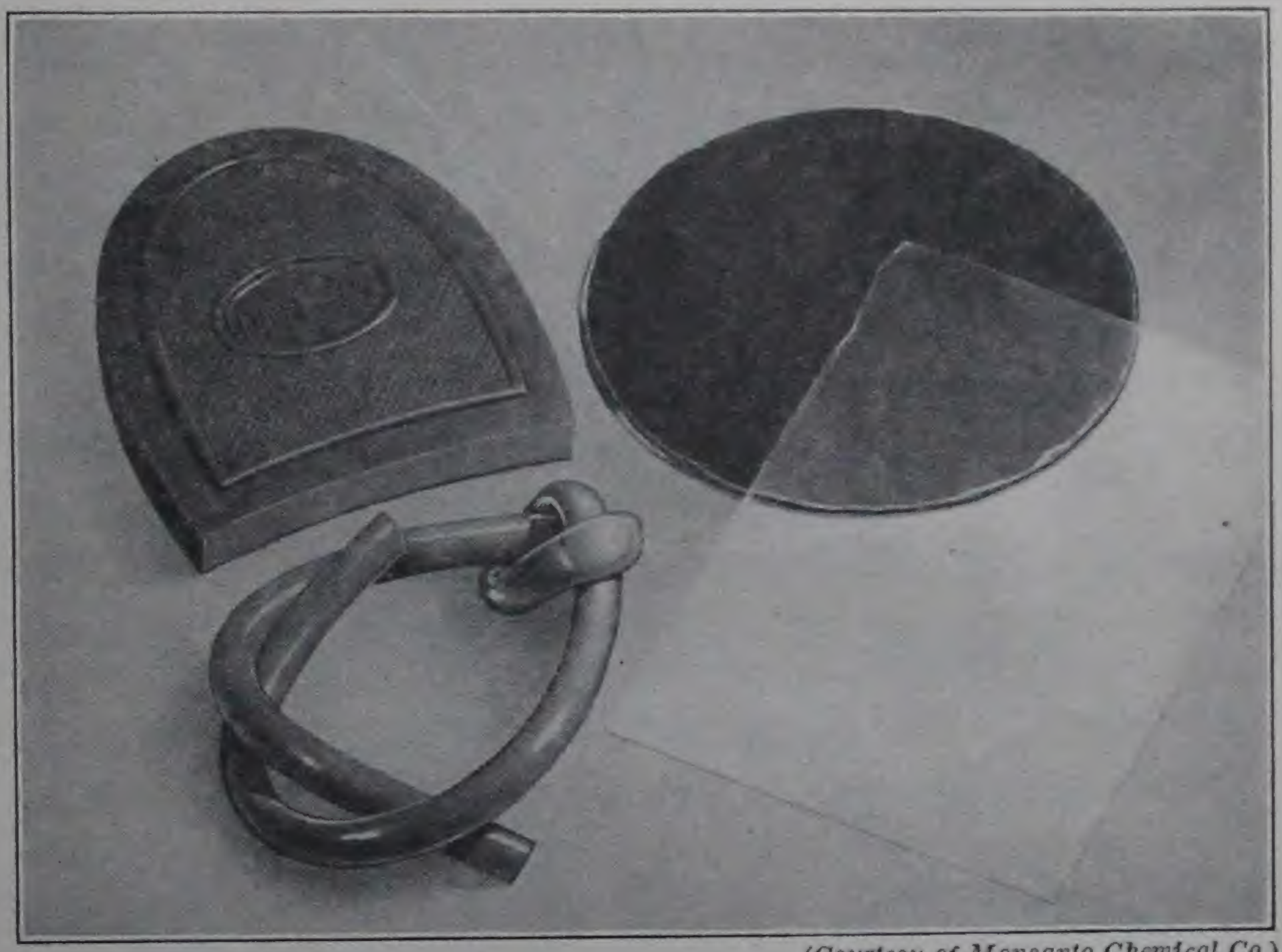


Fig. 7-13. Preparation of Polyvinyl Formal and Polyvinyl Acetal.

Commercially, the hydrolysis and the condensation reaction may be carried out in a single operation. It has been found that better plastic products are obtained if the reactions of hydrolysis and condensation are not carried to completion. Acetyl and hydroxyl groups in the final resin seem to give it some improved properties. The resin is usually recovered from the reaction kettle as a precipitate. The precipitate must be thoroughly washed and dried before it is mixed with other ingredients. Resins formed with formaldehyde are called polyvinyl formals; resins formed with butyraldehyde are named polyvinyl butyrals. However, each manufacturer of a particular vinyl resin has assigned a trade name to his product. Thus, vinyl butyral is better known as Butacite, which has proved to be one of the best materials for the interlayer in safety glass.

7-35. Applications of Polyvinyl Acetals.—The properties of polyvinyl-acetal resins depend on three major factors: the size of the resin molecule, the kind of aldehyde used in the condensation, and the degree of hydrolysis of the polyvinyl acetate. These resins may be plasticized to form molding compositions. They are



(*Courtesy of Monsanto Chemical Co.*)

Fig. 7-14. Some Uses of Vinyl-Acetal Resins.

used as substitutes for rubber in such articles as gaskets, flexible hose, and rubber heels, as illustrated in Fig. 7-14. The unplasticized types are used as impregnating resins for cloth that has largely supplanted the rubber formerly used in making raincoats.

The acetals are very versatile products, as they are tough, adhesive, clear, and chemically inert. They are used in making coated fabrics, plywood adhesives, and household articles. Butyrals, in the form of sheets, foils, or resin solutions, are used in safety glass, adhesives, and cloth coatings. Butyral compounds are molded and extruded into flexible, durable, and gas-proof articles. Some of the trade names are Butacite, Butvar, Saflex, and Vinylite X.

The formals are particularly resistant to the action of hydrocarbons, which may tend to soften or dissolve other types of plastic materials. This property has initiated their use as liners in self-sealing gasoline tanks. Solutions for adhesives, molding compounds, abrasive-resistant coatings for wire insulation, and the like are available.

Chapter Eight

Miscellaneous Plastics

Plastics From Agricultural Products

8-1. Introduction.—A great deal of experimental work is being conducted on agriculatural materials in an attempt to use them for plastics. Some developments have already reached the industrial stage. But none of the materials has as yet attracted much attention or threatens to replace any of the present plastics. Some hold out great promise, whereas others appear to be laboratory curiosities. A general discussion is offered on the more promising ones.

8-2. Bagasse.—Bagasse is the pulpy mass that remains after the juices have been extracted from sugar cane. Chemical analysis of the pulp shows that it contains, among other things, approximately 18 per cent of lignin and 45 per cent of cellulose. It was thought that a combination resin-filler compound could be formed from bagasse without the addition of another ingredient, but results of the first experiments proved that this could not be done. It was found that, if only bagasse resin was to be used, the fiber would have to be destroyed; but, when the fiber was destroyed, the compound lacked strength. Enough resin did not remain to warrant an addition of filler such as wood flour. In the next attempt to produce a plastic, the method was to break down the bagasse into its simple components, the resin and the filler. The resin was much the same as the one separated by the hydrolysis of wood. The pulp minus the resin turned out to be a fairly good filler. The trick was then to mix the resin and the filler. A higher proportion of lignin resin was used, that is, more than the original content of 18 per cent. In this way the results were quite satisfactory. However, the substitution of phenolic resins for bagasse resin was unsatisfactory, because the bagasse filler and the phenolic resin are not entirely compatible.

Bagasse molding compounds are thermosetting, although their "set" is not so hard as that of other thermosetting com-

pounds. In one particular application, this property has turned out to be an advantage. In the molding of threaded closures with this material, the molded piece may be stripped from the mold without cooling and without having to unscrew the closures from the force plugs. The elimination of this operation is a considerable saving in molding time. Once the material has fully set, it never softens again. The final set takes place a few seconds after removal from the mold. Further research is being conducted on combining the bagasse filler with thermoplastic resins in an attempt to make a low cost injection-molding compound.

8-3. Soybeans.—Soybeans contain approximately 40 per cent of protein matter. It was thought that, if casein—a protein substance—could be hardened by an aldehyde, soybean meal could probably be hardened in the same manner. The earliest investigations in the soybean field were conducted by the United States Department of Agriculture. Since the main concern of the department was the utilization of farm products, furfuraldehyde—a product of oat hulls—was chosen as the hardener. A mixture of soybean meal and furfural, which was allowed to stand for several days, hardened into a thermoplastic composition of poor physical and chemical properties. Other experiments involving the use of phenolic resin as binder and soybean meal as filler proved more satisfactory. When phenolic resin was added to aldehyde-hardened meal, thermosetting compounds that were moldable under the same conditions as those used for straight phenolics were obtained. Satisfactory results have been obtained by the use of urea resins instead of phenolic resins, but the urea mixtures have not as yet been commercially produced. Work is constantly being done in an attempt to produce textile fibers from soybeans.

8-4. Zein.—Zein is a protein material that is extracted from corn, about 1 pound of zein being obtained from a bushel of corn. The reaction between zein and formaldehyde is similar to that between formaldehyde and casein, but it takes place more slowly. The slow reaction allows some formaldehyde to be added to the zein before pressing. Their relatively higher absorption makes zein plastics inferior to the caseins. Zein plastics are still in the developmental stage, but their future seems promising in view of their low cost of production. Zein plastics are tough and strong.

8-5. **Shell Plastics.**—A great deal of work has been done on the shells of various nuts. The first shell to be used in the manufacture of plastics was the walnut shell. When the oil has been extracted from the shell, the ground remains have a definite resinous content. The resin is used to augment phenolic resins in the manufacture of a molding compound, as it has been found that a lower phenolic-resin content can be used when the shell flour is used as filler. The shells must be ground fine, or else the resinous content is unreactive.

Peanut shells have been tried experimentally, but their oil content is too high. The shell itself is too fluffy to be used as a filler. Williamson of the United States Department of Agriculture obtained some interesting results when the peanut shell was used as obtained—oil and all. It has been found that pecan and almond shells also contain a resinous body. Some work has been done on both shells, but no commercial plastics have yet appeared. In general, the harder shells seem capable of producing plastics.

8-6. **Flax Shives.**—The shive is the part of the flax seed that is thrown away in the manufacture of cigaret paper. Since the yearly amount of this waste is enormous, it is an ideal raw material for plastics. The shives are ground fine and are incorporated with liquid resins. The flax shives contain certain resinous bodies that permit a lowering of the amount of augmented resin. The method of manufacturing flax-shive plastics is the same as that used for the regular phenol-formaldehyde products. The flax plastics are thermosetting.

A liquid resin product is quite well dispersed, although a calendered product is satisfactorily uniform for many purposes. The primary difficulty is the grinding of the flax shives, as it is not easy to reduce the fibers to the proper size mesh without also destroying some of the strength of the material. Without a doubt, this problem will be overcome, and a successful plastic will result. Experimental tests have proved conclusively that plastics of the flax-phenolic type are equal in all respects to the straight phenolics. Most of the newer agricultural plastics have trouble with cure time. This is not so with the flax compounds, which cure uniformly and as quickly as any other thermosetting material.

8-7. **Oat Hulls and Corn Cobs.**—Good plastic materials are obtained from oat hulls and corn cobs. Since furfural is derived

from oats, it seems only natural that the complete plastic should be derived from the oat hulls. Both the cobs and the hulls contain certain natural resins along with the mealy body. When such resins are combined with resins of the phenolic type, good general-purpose plastics result. The resinous bodies in the cobs and hulls permit a lowering of the augmenting resin in the compounding stage. The plastics are completely thermosetting; and, while their properties are not so good as those of the flax-shive plastics, they are satisfactory for ordinary use.

Miscellaneous Resins

8-8. Columbia Resins.—The name *Columbia Resins* has been given to a broad family of chemical compounds containing only hydrogen, carbon, and oxygen. Such resins are entirely thermosetting. The unusual property of these compounds is that they are crystal clear, their optical properties being said to be superior to those of cast methacrylate. The refractive index of one of the Columbia Resins, C. R. 39, is 1.505, as compared to 1.52 for plate glass and 1.49 for cast methacrylate. Monomeric C. R. 39 is a clear, colorless liquid at room temperatures. The addition of heat and a catalyst, such as benzoyl peroxide, changes the monomer to the polymer. Variation of properties in the polymer is not achieved by adding plasticizer but results from the adjustment of the molecular structure.

At the present time, the Columbia Resins are available only as clear cast sheets and as laminating binders. Further research is under way to produce the compound as a molding resin. The results of this research will be very interesting, because, if such a resin proves successful, the industry will get its first crystal-clear thermosetting molding compound.

8-9. Vinsol.—Vinsol is the trade name given to a thermoplastic resin obtained by steam distillation of Southern-pine chips. The resin is not suitable for plastic molding compounds by itself, but its compatibility with a wide variety of cellulose derivatives and natural resins has made it of great value to the plastics industry. No synthetic or natural material has been produced as an exact substitute for shellac, but Vinsol come very close to being one. In both electrical and physical properties, Vinsol very nearly

approaches shellac. Formulas 1 and 2 are both commercially accepted plastics.

Formula 1	*Per Cent*
Vinsol	70
Ethyl cellulose	25
Castor oil	5

Formula 2	*Per Cent*
Vinsol	65
Cellulose acetate	18
Dimethyl phthalate	17

Vinsol reacted with formaldehyde produces a resin that is compatible with phenol-formaldehyde resin, and this Vinsol resin has been successfully incorporated into some phenolic formulations. In phonograph records, Vinsol has almost completely replaced shellac as the binder. The records are not so long-wearing as shellac records, but Vinsol kept the industry alive when shellac was not allowed to be used for phonograph records because of war-time restrictions.

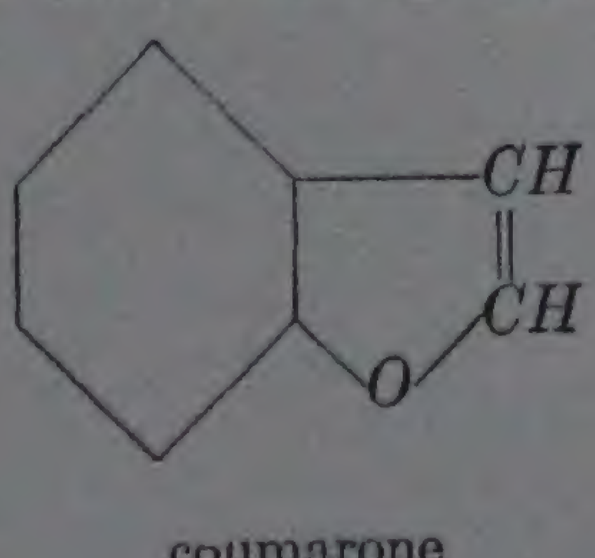
Vinsol is insoluble in petroleum and vegetable oils. This factor has opened the protective-coating field to Vinsol for specific uses. Vinsol has recently been used to impregnate paper that is used in the manufacture of rigid tubing. The trade name *Fedralite* has been given to fiber products modified with Vinsol.

There are many other natural resins that are in the experimental stage of development into plastics. None has reached the production stage, or been commercially used in plastic formulations.

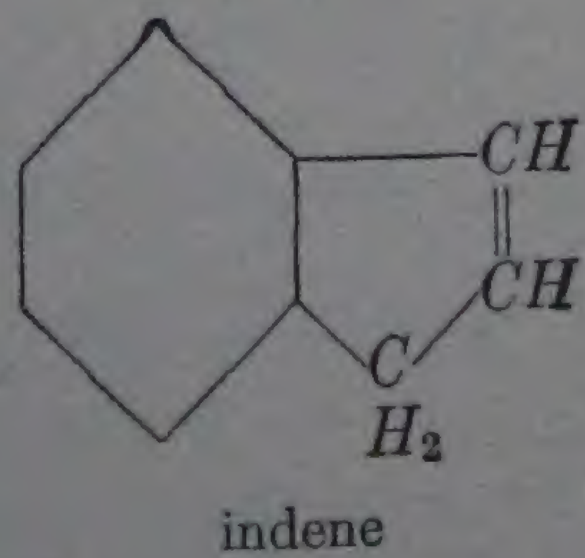
8-10. Alkyds.—The alkyd resins are polyesters, each being the product of a condensation reaction of a polybasic acid and a polyhydric alcohol. The most frequently used acid is phthalic acid, and the almost universally used alcohol is glycerol. The anhydride of the acid is generally preferred to its other forms. Since there are many polybasic acids and many polyhydric alcohols, it follows, therefore, that many different kinds of alkyd resins are possible. The word *alkyd* combines the *al* of the word *alcohol* and the *cid* of *acid*. The pronunciation *al-kid* was accepted as being more euphonious, and so the spelling was changed accordingly. Phthalic anhydride is commercially obtained from naphthalene by catalytic oxidation. Glycerol, or glycerin, is a by-product in the manufacture of soap, resulting from the hydrolysis of fats and oils. Glycerin may also be obtained from the fermentation of glucose.

Although alkyd resins are thermosetting and they may therefore be used as compression-molding powders, their better known applications are as paints and protective coatings. The conventional mixing and rolling methods, by which lubricants, fillers, plasticizers, and accelerators are incorporated, work well on the resin, but the plastic molds poorly. The alkyds excel in the coating industry. In this case, modifying agents such as drying oils, solvents, natural resins, and fatty acids are all made part of the primary reaction, and so are placed in the kettle with the acid and the alcohol. The condensation product varies with the raw materials used. With plasticizers and solvents, the resin is usually a liquid, which may be dispersed in water to form a water-emulsion paint. The pure condensation resin without these modifying agents is soluble in a variety of organic solvents, the solutions of which go into lacquers and adhesives. Notwithstanding, the alkyds are compatible with a wide variety of synthetic and cellulosic resins. Like the phenolics, the alkyds pass through the A-stage and the C-stage in polymerizing. Alkyd-modified phenol-formaldehyde materials are available for special uses. Glyptal, Dulux, Amberlac, Rezyl, Teglac, and Beckosol are some of the more common trade names of alkyd resins.

8-11. Coumarone-Indene Resins.—Like the alkyds, the coumarone-indene, or coal-tar, resins are less suitable as principal plastic compounds than as modifying agents for other plastic materials or as adhesive cements. Coumarone and indene are found together in the naphtha fractions of coal-tar distillates. Naphtha is treated with sulfuric acid to extract the resin, which remains in solution with the acid. The structures of coumarone and indene show that they contain vinyl-substituted groupings, and so the mechanism of their polymerization is similar to that of other vinyl compounds. Coumarone and indene have the structural formulas shown in Fig. 8-1.



coumarone



indene

Fig. 8-1. Structures of Coumarone and Indene.

Coumarone-indene resins are compatible with almost every plastic material. They are used to modify phenolic compositions and the vinyl resins. These coal-tar resins have proved unsatisfactory when molded because of loss of strength and a tendency to stick to the mold. Addition of filler aids in solving the sticking problem but decreases the mechanical strength. The resins, which are soluble in a variety of common solvents, are used as softeners in the reclaiming and milling of rubber. Solutions of the resin modified with plasticizers are used for varnishes and printing inks. Mastic floor tiling in a variety of colors is being produced exclusively with coumarone-indene resin plasticized with tung oil. The tile is resistant to alkali soaps, ammonia, and some acids. Some of the common trade names associated with the resins are: Cumar, Nevillite, and Nevindene.

Chapter Nine

Plastic Textile Fibers

Synthetic Resin Fibers

9-1. Classification of Fibers.—All the materials mentioned up to this point are connected with the plastic industry through some form of molding. Many of the materials are available in forms other than molding compounds, but always the main usage of the material is molding. Many other materials are basically plastic but are not associated with the plastic industry because they are used in some other well-established industry. Synthetic rubbers and synthetic textile fibers fall into this category. The fact remains that these materials are plastics and their study should be included in any plastic literature.

The materials making up the plastics-textile-fiber group are, in a great many instances, the same as those used in the molded plastics. In some cases, special materials were developed for fibers alone. As a general rule, a compound that is satisfactory as a fiber can be converted into a molding compound. The reverse is definitely not true. All textile fibers of a plastic nature are thermoplastic. There are three groups:

1. Synthetic resin fibers
2. Rayon fibers
3. Fibers from natural materials

The synthetic resin fibers include nylon, vinyon, and saran. Rayon fibers are made from cellulose. Natural materials used for fibers are protein and glass.

9-2. History of Nylon.—The groundwork for the discovery of nylon was laid in 1928 by Carothers, who began the study of the structure of substances having high molecular weight for the purpose of adding to the chemical knowledge of these substances, which were so little understood. By making polymer after polymer with various organic chemicals, such as dibasic acid amides and glycols, he obtained a better understanding of polymers. Soon the

evolution of superpolymers that would approximate silk, wool, and other natural protein substances was being predicted. Attention was directed toward a polyamide that might form the basis for a commercial textile fiber. On February 28, 1935, the superpolymer from hexamethylenediamine and adipic acid was first synthesized. The resulting polymer was called "66," the first 6 indicating the number of carbon atoms in the diamine and the second 6 the number of carbon atoms in the dibasic acid. Later, however, the polyamide was given the name *nylon*. Nylon is not chemically identical with silk, and so it would be misrepresented if it were labeled as synthetic silk.

9-3. Chemistry of Nylon.—Nylon is a thermoplastic linear polyamide. It is made by the reaction of a dibasic acid with a diamine. The present textile fiber is made by first reacting adipic acid with hexamethylenediamine, and forming the corresponding salt, as indicated in Fig. 9-1.

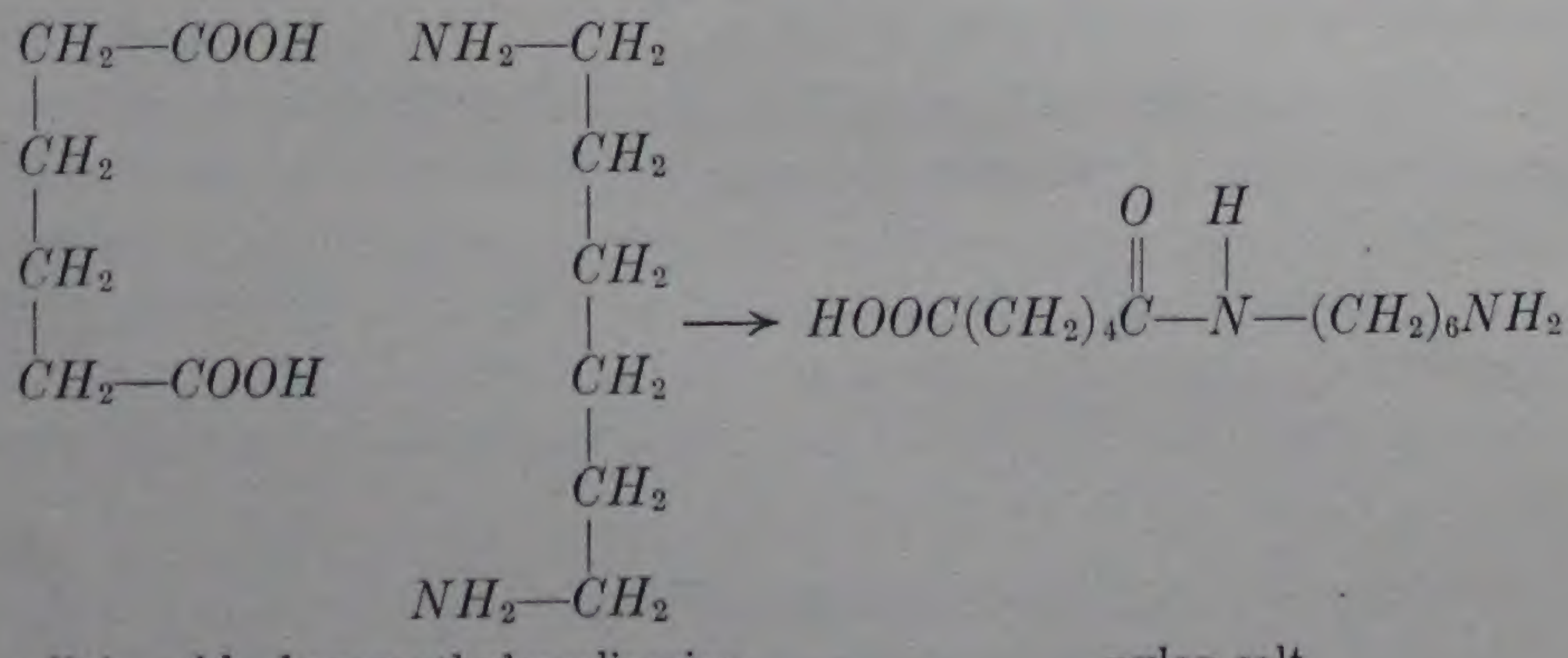


Fig. 9-1. Formation of Nylon Salt.

The salts are charged and heated in a pressure vessel, where they are caused to polymerize. A section of the polymer chain would have the structure shown in Fig. 9-2. An examination of the

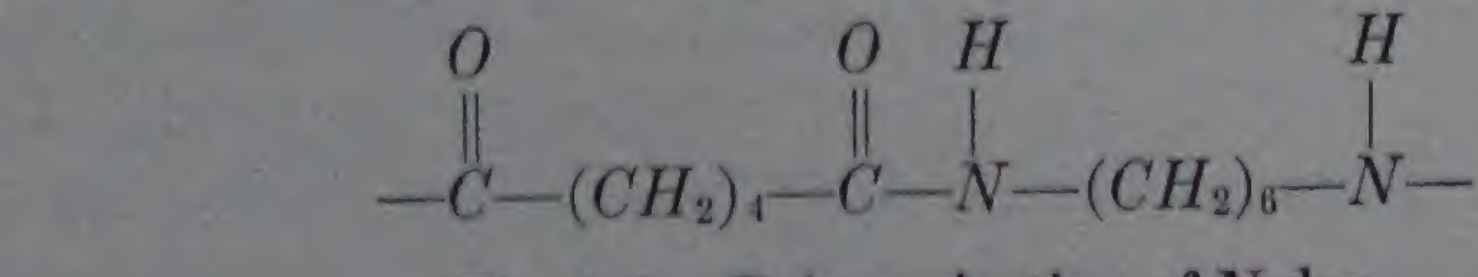


Fig. 9-2. Polymerization of Nylon.

long-chain polymer has shown molecular weights of 10,000 and higher.

9-4. Raw Materials for Nylon.—The raw materials used in the production of nylon consist of coal, air, and water. The phenol and phenolic derivatives in nylon come from the coal; the nitrogen is taken from the air; and the hydrogen is supplied by water. Nylon is a class name for a group of substances, and no definite formula can be assigned to it.

There is no need for lubricants, accelerators, or retarders in making nylon, but small amounts of finely ground pigments such as titanium dioxide are sometimes added to impart a dull finish to the extruded fiber, which ordinarily has a high luster.

9-5. Manufacture of Nylon Flake.—Since practically all linear polyamides will produce a material capable of making a fiber, many different nylons can be prepared from various kinds of dibasic acids and diamines. Diamines and dibasic acids may react at both their ends. This property makes it possible to react two different diamines with one dibasic acid, or to react two dibasic acids with one diamine. The number of nylons is as limitless as the number of different chemical combinations that are possible from its basic ingredients.

In Fig. 9-3 is shown a flow chart for the production of nylon. A diamine and a dibasic acid are mixed to produce an amide salt in a water solution. As a result of heat polymerization in a pressure vessel, a polymer that resembles a tough hornlike mass is obtained. The molten nylon is extruded as a ribbon onto a large revolving wheel. The strands are cooled by a spray of cold water to solidify them and prevent sticking. Later the strands are chopped up into fine granules or chips. This material is known as nylon flake, which may be used directly as an electrical insulating material or as a molding compound.

9-6. Extrusion of Flake.—If a monofilament or bristle fiber is needed, the nylon flake must undergo further processing. The chips are remelted and are put into a special vertical hopper, where the delustering agent is added. A spinneret, which is a metal disk with very fine holes through it, is attached to the hopper so that the molten material leaving the hopper is forced to pass through the spinneret. The material comes from each hole in the spinneret in a continuous stream. This material solidifies as soon as it hits the air and, in doing so, forms a continuous filament.

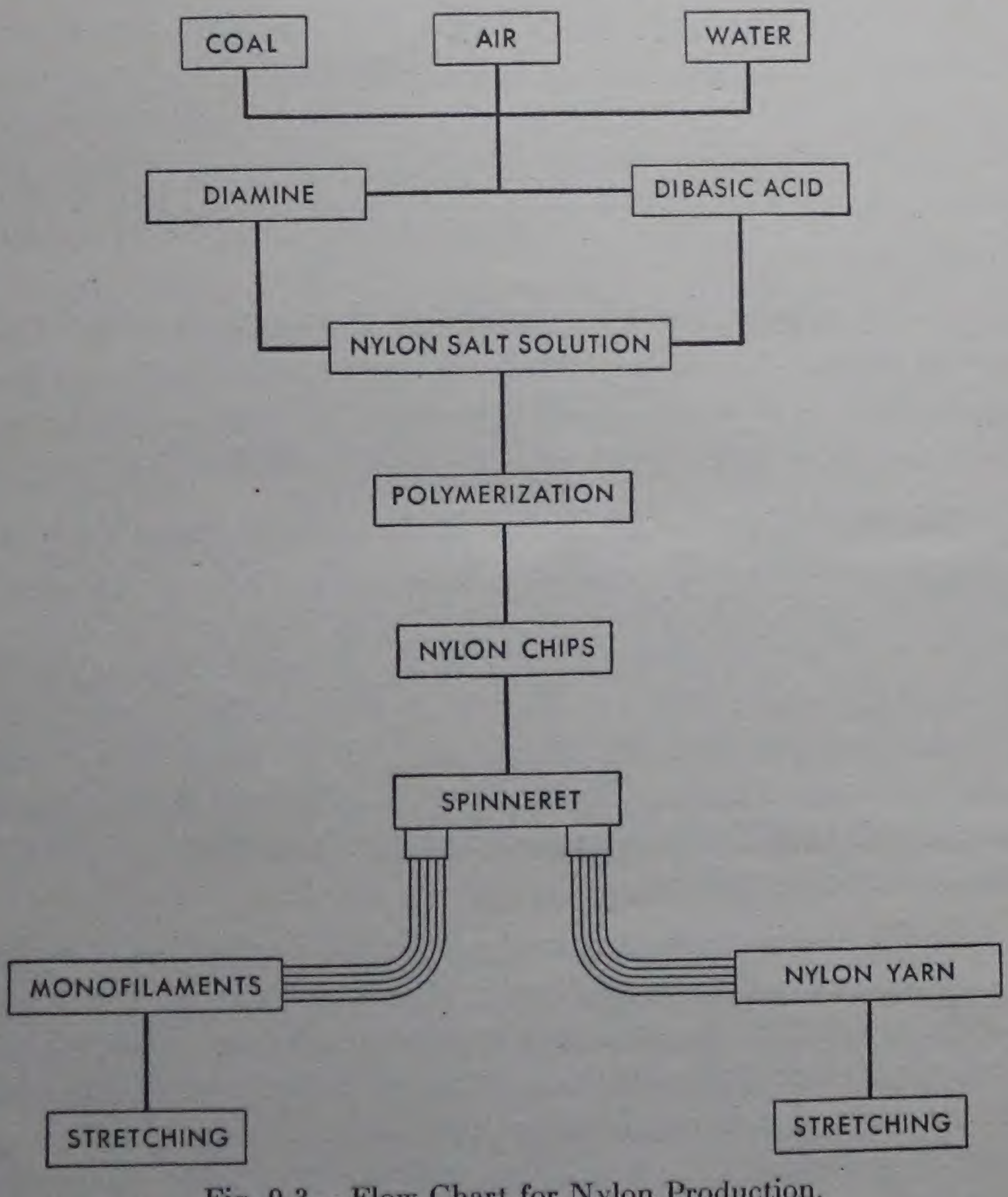


Fig. 9-3. Flow Chart for Nylon Production.

The size of the filament is determined by the speed at which the polymer is fed and by the rate of withdrawal of the filament. Many filaments are converged into a single strand, which is wound on bobbins. When the material is to be used for bristles in various kinds of brushes, enough individual filaments are brought together to give the desired thickness. The bristle fiber is not wound, but is immediately cut to size and is tied into bundles.

9-7. Crystallinity of Nylon.—An X-ray picture shows the structure of nylon to be crystalline. The molecules are entirely unoriented, in which condition they have very little strength. It is necessary to cold-draw, or stretch, the fiber to achieve ultimate strength. The filament that is wound on the bobbin is soaked in

water and then stretched. The stretched fiber is called nylon yarn. The stretching is done by simply winding the filament onto another bobbin at a greater speed than that at which it is being unwound. The filament may be stretched as much as eightfold, although the usual stretch is only fourfold. A fourfold stretch reduces the diameter to one-half the original diameter. During the stretching process, the molecules become lined up parallel with the axis of the fiber. With the molecules oriented, the fiber possesses strength that is greater than that of silk or rayon. Since the delusterizing agent is added to the molten polymer before it goes through the spinneret, the stretched fiber has no luster.

9-8. Properties of Nylon.—Nylons are crystalline materials with definite melting points. The nylon used for textile yarn has a melting point of about 480° F, but other nylons may have melting points of 600° F or higher. The melting point depends entirely on the chemical composition of the nylon. Nylon is wet by water, but the amount of water absorbed is only 3.5 per cent.

TABLE 9-1

WATER ABSORPTION OF TEXTILE FIBERS

Fiber	Water Absorption Per Cent
Nylon	3.5
Acetate rayon	6.5
Silk	11.0
Viscose rayon	12.0
Wool	13.0
Vinyon	0.0

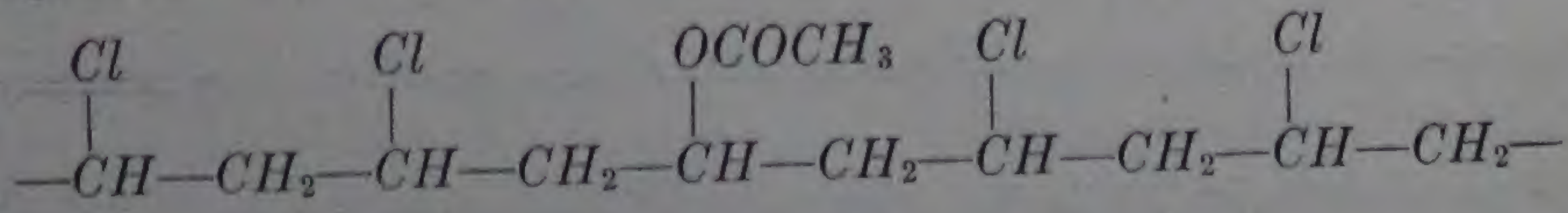
As shown in Table 9-1, the water absorption of nylon is much lower than that of any other textile fiber except vinyon. It is this low moisture absorption that allows a pair of nylon stockings to dry so rapidly. Bristles made from nylon filaments rarely become soft and flabby during washing as other fibers do. Nylon yarn is completely resistant to cleaning fluids and common chemicals. The nylon flake is, in general, unaffected by acids and alkalies, although oxidizing acids cause decomposition. Nylon yarn for all practical purposes is stable toward light and resists the growth of fungi. Moths are not attracted to nylon fabrics.

The toughness of nylon exceeds that of any other fiber, synthetic or natural. Toughness varies in a fiber from the wet to the dry condition, a dry fiber being more tenacious that a wet one. Nylon fibers when wet are stronger than rayon or silk in the dry state. Nylon yarn will stretch when under stress, but the elastic recovery value is 100 per cent. This means that nylon fabrics will always return to their original form after being stretched. No other textile fiber has a practical recovery value of 100 per cent.

9-9. Uses of Nylon.—Nylon is used for many things besides women's hosiery. The yarn has replaced the yarn formerly used in bait-casting lines, sewing thread, fly lines, braided surgical sutures, and shoe laces; and nylon threads have replaced the silk threads formerly used in United States currency. Clothing may be knit or woven of nylon yarn. A nylon fleece that is soft, light, and warm has been successfully produced.

Larger filaments, called monofilaments, are used for bristles in toothbrushes, industrial brushes, and vacuum-cleaner brushes, and in insect screening and tennis-racket strings.

9-10. Chemistry of Vinyon.—The basic ingredient of vinyon is an unplasticized vinyl resin, a copolymer of vinyl chloride and vinyl acetate. A copolymer consisting of from 85 to 90 per cent of vinyl chloride and from 15 to 10 per cent of vinyl acetate is the type that is made into filaments. The chain polymerization contains two chlorides to one acetate, as shown by the following structural formula:



9-11. Method of Manufacture.—The copolymer is ground to a powder having the consistency of flour. The resin is dissolved in a measured amount of acetone, and the solution is filtered and stored at 50° C in large aging tanks, where entrapped air bubbles are allowed to escape. The filtering operation is an important one, since vinyon is a spun fiber and any foreign matter would have a tendency to clog the holes in the spinnerets. A constant temperature must be maintained throughout the 24-hour seasoning period, because the solution has a tendency to form a gel when cold. The

solution at this stage is called "dope." It is a heavy, thick liquid resembling clear corn syrup.

The syrup, after seasoning, is ready for spinning. In this operation the viscous syrup is placed in a container from which it can be extruded through a spinneret. The holes in the spinneret are about .002 to .005 inch in diameter; that is, they are so fine that a strong light can barely be seen through them. After a vacuum has removed all the air from the syrup and the apparatus, air under pressure is used to force the syrup through the spinneret and downward through what is called a spinning cell, which is simply an elongated box or tube through which warm air is circulated upward. The warm air evaporates the acetone, and the resin coagulates into a continuous filament. This process is known as dry spinning.

The individual fine fibers are gathered together into a thread, which is immediately stretched. As many as forty or fifty filaments may go into a single thread. The stretching operation, which orients the molecules and definitely increases the tensile strength, must be performed with extreme care. The threads are then oiled and twisted for free slippage and further alinement. Oiling the yarn allows a good sliding action when the yarn is passed over drums and bobbins in further processing. Oiling also reduces the hazard of breakage. Twisting the yarn enhances its strength and, in addition, brings the molecules into further alinement much the same as in the stretching process.

9-12. Properties of Vinyon.—Vinyon is definitely thermoplastic. Temperatures over 65° C cause shrinkage, the effect varying with the temperature. At 70° C the shrinkage is about 7 per cent, while a temperature of 140° C causes tackiness and softening of the fiber. The yarn will burn but will not support combustion. The fact that vinyon is completely and permanently water resistant makes it ideal for shower curtains and similar applications.

Vinyon is light stable, and sunlight has little or no effect on it. It absorbs dyestuffs easily, and a wide variety of colored yarns and fabrics is available. In the natural state, vinyon has a high luster, which can be toned down by the addition of small amounts of pulverized earth pigments in the spinning dope.

Vinyon is an excellent chemical-resistant material. Concentrated sulfuric and nitric acids have no effect at all on fibers made

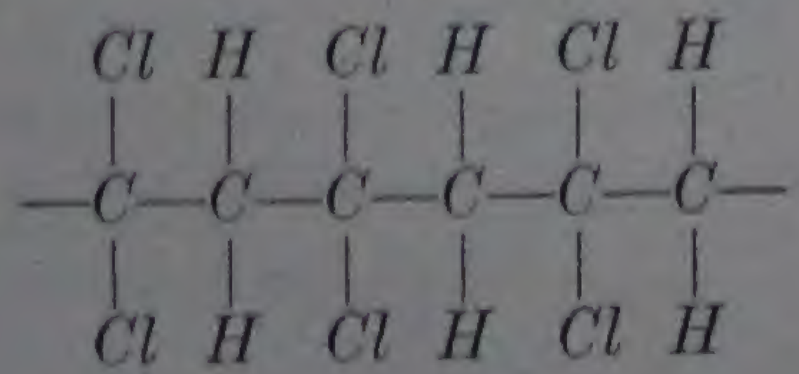
from this material. Vinyon is also resistant to aliphatic hydrocarbons and alcohols, but is attacked by esters, ethers, and ketones. Bacteria and plant growths do not have any effect on the stability of vinyon.

Tensile strength in textile fibers is measured in grams per denier. The denier of a yarn is the weight of 450 meters of the yarn at standard conditions expressed in units of .05 gram. The tensile strength of nylon is expressed as 5 grams per denier, while that of vinyon is about 4 grams per denier. Silk is between the two; however, silk falls below the 4-gram mark when wet. Nylon also loses some of its tensile strength when wet. Vinyon maintains its tensile strength whether in the dry or wet state.

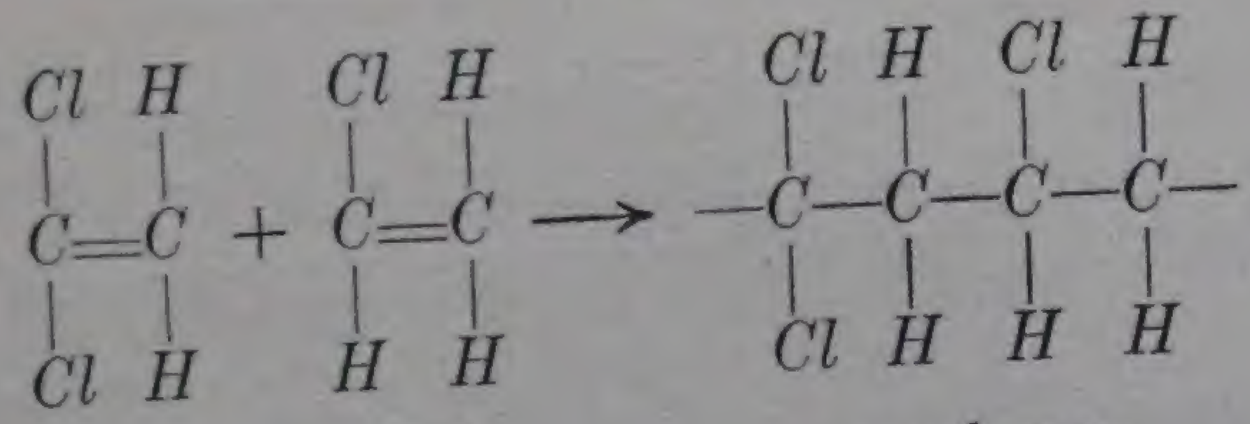
9-13. Uses of Vinyon.—Vinyon is available as yarn only. It exhibits all the necessary qualities for a good throwing and knitting material. The following uses have been devised for it: Shower curtains, dental floss, gloves, woven shoes, and other articles of clothing. It is almost a certainty that hosiery will be made from vinyon.

9-14. History of Saran.—Resins containing vinylidene chloride, whether polymers or copolymers, have been given the name *Saran*. Vinylidene chloride was discovered at the time when the use of plastic materials was being expanded. It was natural, therefore, that research be done on the use of vinylidene chloride as a fiber. The material is produced as a monofilament, but its use as a yarn is secondary in importance to its use as a molding compound.

9-15. Chemistry of Saran.—Vinylidene chloride polymerizes in a long straight chain, which can be represented by the following structural formula:



A mixture of vinylidene chloride and vinyl chloride may be made to copolymerize in the following manner:



As was stated in the previous discussion of vinylidene-resin polymers, a wide range of compounds can be formulated with correspondingly different physical properties. Compounds of higher softening points show a greater degree of crystallinity. Aside from its use as a plastic material, Saran is being marketed as monofilaments that are round or odd-shaped in cross-section.

9-16. Method of Manufacture.—Saran, when first extruded and cooled, is amorphous. As the material stabilizes to room temperature, it crystallizes. Under ordinary extruding and cooling conditions, the crystallization is a random process; but, by carefully regulating the extruding and cooling temperatures, the crystallization can be controlled. This control results in an orderly arrangement of molecules. As is the case with other plastics, orienting of the molecules produces a stronger product.

Saran fibers are manufactured by the extrusion process. Furthermore, Saran is the only synthetic resin that is made into monofilaments by straight machine extrusion without the aid of solvents. The material is extruded continuously through a warm die, the temperature of which must be above the crystallizing temperature of the material. There is a marked difference between the cooling temperature and the crystallizing temperature of the material. The uncrystallized extruded Saran is run through a water bath, the temperature of which is rigidly controlled so as to retard crystallization. At this stage, the material is amorphous and can be stretched and worked. As the material leaves the water bath, it slowly crystallizes, but the stretching has served to orient the crystal formation. An unoriented filament might possess a tensile strength of 4,000 pounds per square inch, whereas an oriented filament might have a value of 13,000 pounds per square inch. The stretched filaments are either wound on coils or cut to length, the procedure depending on its ultimate use.

9-17. Properties of Saran Fibers.—In almost all cases, the oriented Saran fibers show properties superior to those of the unoriented fibers. All properties discussed here refer to the oriented fibers.

As with almost all vinyl resins, the moisture absorption is low. The published record states that the figure is .5 per cent. This places Saran fibers almost on an equal level with vinyon. Saran is resistant to all common chemical solvents such as aromatic and aliphatic hydrocarbons, alcohols, and ketones. It has a good resistance to dilute alkalies, but is attacked by concentrated ammonia. Acids, either diluted or concentrated, have little effect on it. Saran fabrics are not stained by ink.

Saran has excellent mechanical strength in both the wet and the dry states. It is a good weathering material, for sun, rain, and cold have little effect on its dimensional stability. The material is available in a wide range of colors and mottled effects.

9-18. Uses.—Fabrics woven of Saran filaments are rather harsh, porous, and waxy. However, a finishing operation that consists in flattening the fibers by pressure calendering improves the appearance and touch. Saran fabrics are used in upholstering the seats of automobiles, street cars, and trains, and in drapes, belts, braces, and other trimming effects.

A tubular Saran braid is employed effectively as fly-screening, because of its exceptional durability on exposure to salt air, corrosive fumes, and the like. Dog leashes, ropes, and assist cords, and robe rails in automobiles, have been made of Saran.

Rayon Fibers

9-19. Classification.—Rayon is the generic term for all fibers and yarns made from or with cellulose as a base, and for the fabric made from these yarns. It is not the name for a single substance, but is the name for many materials of the same chemical nature. There are several methods of classifying rayon. The first method divided rayon into two classes according to the nature of the fibers produced. In this classification the two categories are regenerated cellulose and cellulose derivatives. The second method divides rayon into four groups according to the chemical process used in its production. The four categories of this classification are viscose, nitrocellulose, cuprammonium, and cellulose acetate.

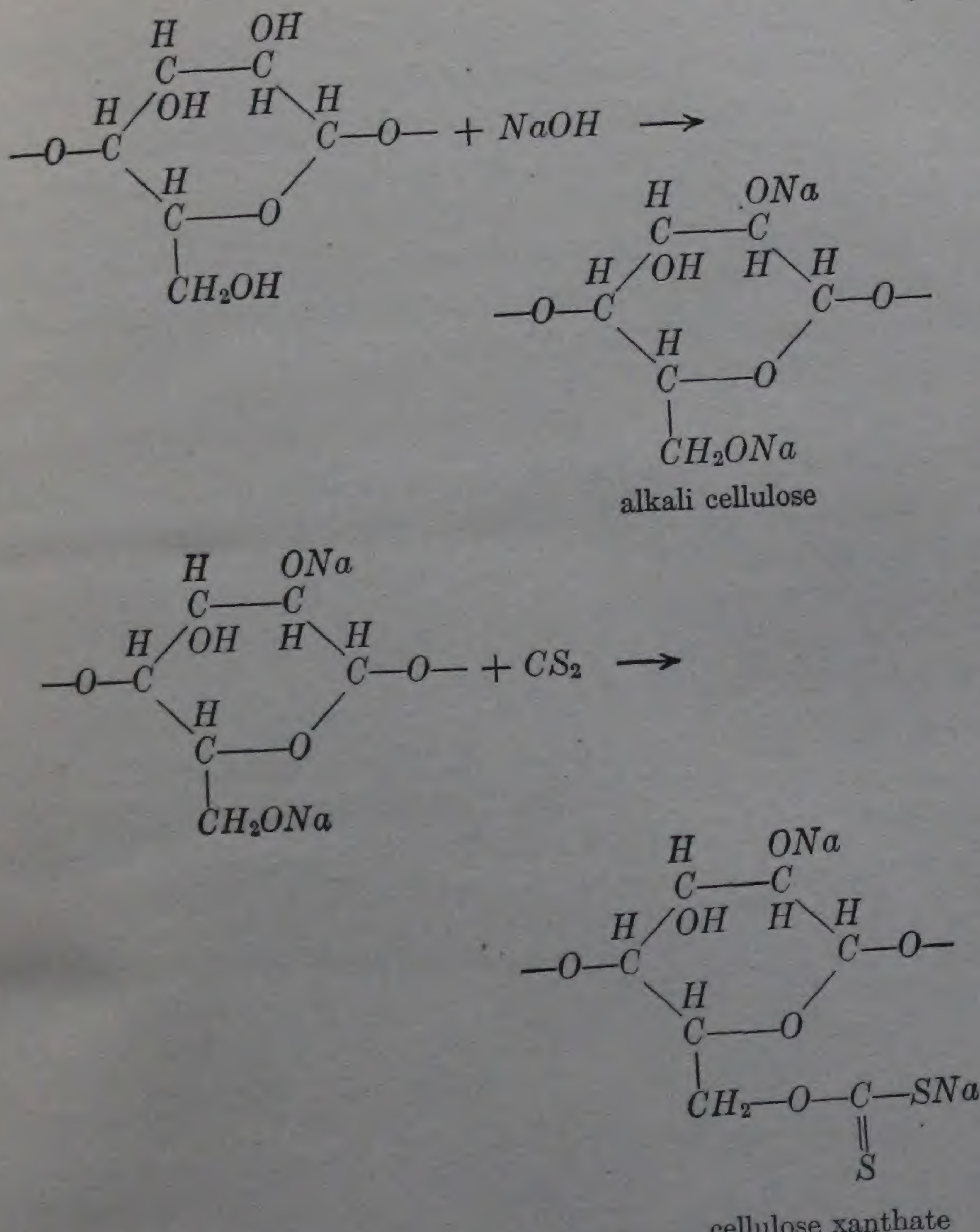


Fig. 9-4. Reactions in Production of Cellulose Xanthate.

Both methods provide satisfactory classification, but the second one will be discussed, as it is the simpler. In terms of the first method of classification, the viscose, nitrocellulose, and cuprammonium rayons are regenerated cellulose, whereas cellulose acetate is a cellulose-derivative rayon.

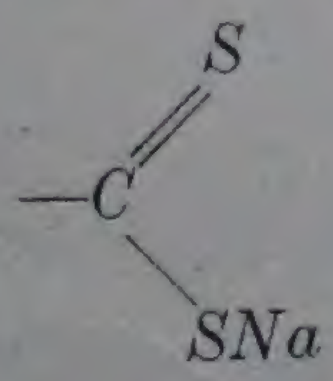
9-20. History.—Audemars, a Swiss chemist, experimented with nitrocellulose as early as 1855, taking out a patent on the transformation of nitrocellulose into fine threads. In 1877, Joseph Swan produced fibers by squeezing collodion (nitrocellulose dis-

solved in a mixture of ether and alcohol) into a coagulating bath. In 1884, de Chardonnet obtained a French patent for the production of fibers from cellulose, but he did not begin commercial production until 1891. In 1892 the English chemists Cross, Bevan, and Beadle discovered another process, the viscose process. In the same year Cross and Bevan discovered the straight cellulose-acetate rayons. Since that time many others have contributed to the development which has placed the synthetic fiber industry in the position it occupies today.

9-21. Chemistry of Viscose Process.—One of the methods of producing regenerated cellulose is the so-called viscose process. In this process cellulose from wood pulp or cotton linters is treated with alkali and carbon disulfide to form cellulose xanthate. The purpose of converting the cellulose to the xanthate is to obtain a cellulose solution that can be easily extruded into filaments.

Treating a cellobiose unit of cellulose with alkali results in the formation of alkali cellulose. On addition of carbon disulfide to the alkali cellulose, cellulose xanthate is formed. These chemical transformations are shown in Fig. 9-4.

A small amount of water is added to cellulose xanthate to form a thick solution known as viscose. This may be converted into threads of regenerated cellulose by extruding through a spinneret into an acid solution, which removes the xanthate group,



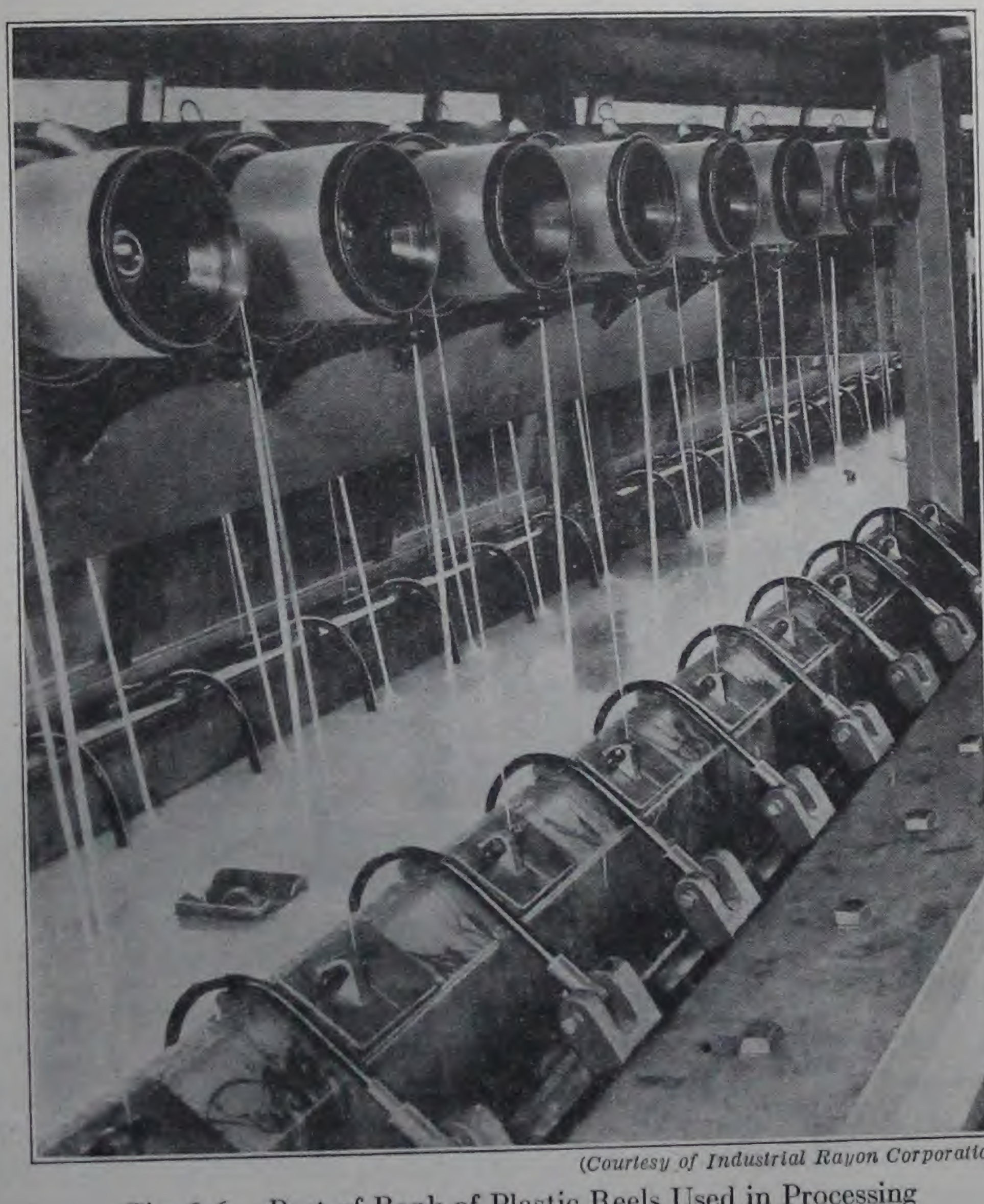
9-22. Raw Materials.—Viscose is a thermoplastic rayon of the cellulose type. Since cellulose obtained from wood pulp produces a better fiber than the cellulose obtained from cotton, wood pulp is the basic raw material for the manufacture of viscose. Wood pulp is mixed with acids and live steam, and the mixture is brought to a boil. The process, which is usually referred to as digestion, produces pure cellulose by removing resins, gums, and other foreign matter from the wood pulp. After leaving the digester, the cellulose is thoroughly washed to free it of acid. It is then whitened by a bleaching operation.

(Courtesy of Industrial Rayon Corporation)

Fig. 9-5. Spinneret for Production of Viscose.

9-23. **Preparation of Viscose.**—The bleached pulp, as a rule, is run through rollers to form sheets. The sheets are soaked for several hours in a caustic-soda solution in order to convert the cellulose to an alkali cellulose. The sheets are then removed from the alkali tank and are pressed to get rid of excess alkali. The pressed sheets are placed in a sigma-type mixer, where they are torn apart and ground to fine crumbs. This mixer derives its name from the fact that the blades are shaped like the Greek letter sigma, Σ. The crumbs are aged for several days to stabilize them with the atmospheric conditions. The aging period also permits all particles of alkali cellulose to become uniform in composition.

The crumb alkali cellulose is placed in a rotary mixer with a measured amount of carbon disulfide. The mixture is slowly churned, and cellulose xanthate is formed. The xanthate is light orange and, except for the color, looks the same as the crumb



(*Courtesy of Industrial Rayon Corporation*)

Fig. 9-6. Part of Bank of Plastic Reels Used in Processing Thread in Rayon Plant.

alkali cellulose. Chemically, however, a great change has taken place, since the xanthate is soluble in water. The crumb xanthate is mixed thoroughly with dilute caustic until a thick viscous mass, called viscose, is obtained. The viscose must be filtered to remove all foreign matter, as even a small speck of dirt would clog the spinneret holes. The tank is also placed under vacuum to remove air, because it is possible that even an air bubble may cause a break in the spinning process.

9-24. **Production of Yarn.**—The viscose is fed from the tank to a pump, which regulates the speed of spinning and forces the

viscose through a filter and then through a spinneret, shown in Fig. 9-5. The holes in the spinneret are from .002 to .005 inch in diameter, being almost invisible to the eye. The spinneret is immersed in a mild acid bath. As the viscose is forced through the spinneret, it comes in contact with the acid, which immediately hardens the solution and reverts it to pure cellulose filaments. The fibers are collected, and the yarn thus produced is wound on a spool. The plastic guides below the reels in Fig. 9-6 strip the threads of excess moisture. The yarn is then washed to remove any excess acid, dried, and rewound onto another spool. During the rewinding, the fiber is twisted and stretched to give it additional strength.

Instead of being twisted when it is rewound, the rayon may be box spun. Box spinning is a process in which the yarn is twisted as it leaves the spinneret, and, instead of being wound on a spool, it is simply coiled into a revolving cylinder.

The yarn at this stage is gleaming and bright. If a dull fiber is required, a small amount of finely ground pigment must be incorporated into the spinning solution. The yarn must be washed and bleached before it can be marketed. Chemical washing removes the sulfur from the yarn, and bleaching turns the yarn pure white. At this stage, the yarn is chemically the same as the starting cellulose, but, instead of being a pulp, it is a tough fiber. It is this fiber that is used to make fabrics.

9-25. Uses of Viscose.—One of the more important uses of viscose rayon is for the making of tire-cord fabric. As a fabric material, viscose has a variety of uses. It can be dyed easily with standard dyes, and all colors are possible.

9-26. Nitrocellulose Rayon.—The nitrocellulose process of making rayon is now practically obsolete, but it is worth noting for a comparison with modern methods. Cotton, which is chiefly cellulose, is treated with a mixture of nitric and sulfuric acids to form the nitrated compound. This compound is dissolved in a mixture of alcohol and ether to form a syrupy solution, which is filtered to remove impurities. By forcing the filtered solution through glass capillary tubes, a fiber is formed; and this fiber is passed through a hot-air chamber. The hot air evaporates the solvents and precipitates a nitrocellulose fiber, which is inflammable. An ingenious denitration process was evolved to remove the

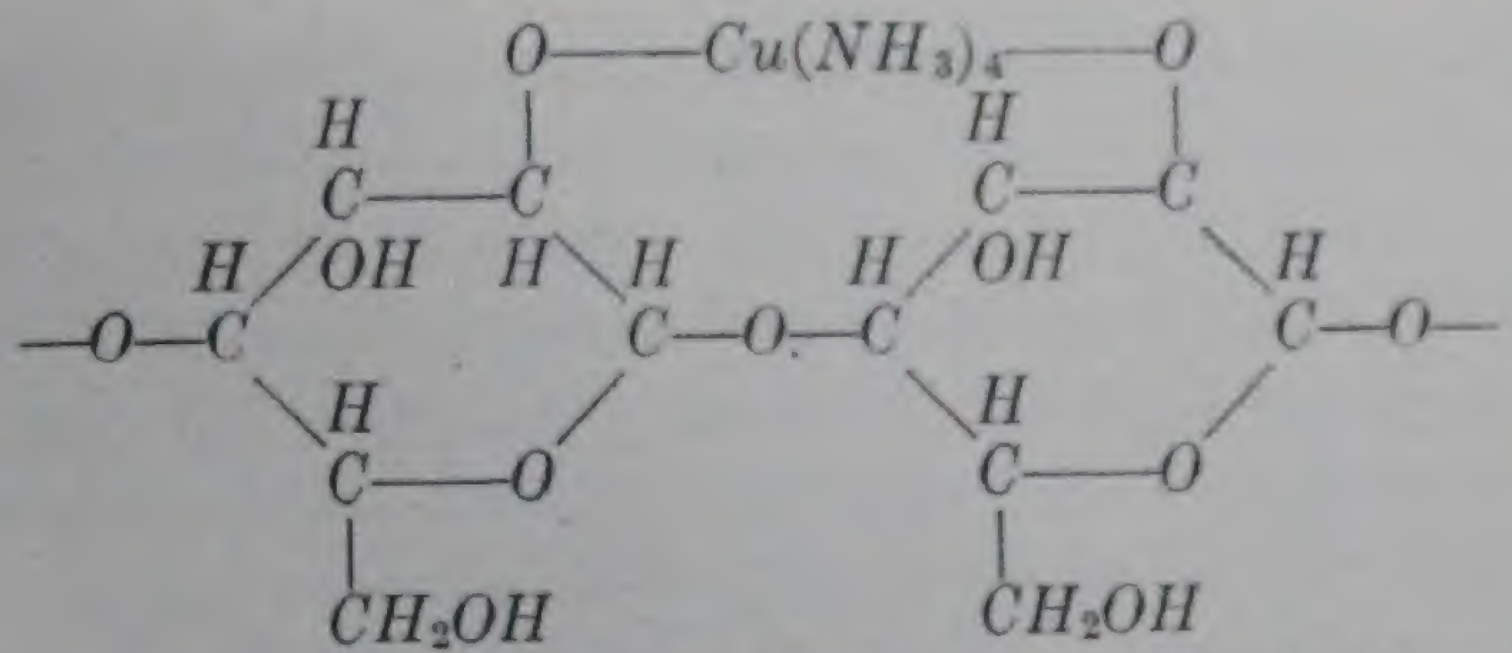


Fig. 9-7. Form of Cellulose in Cuprammonium Solution.

nitrate radicals and produce a regenerated cellulose fiber. Denitration is accomplished by bathing the fiber in a hydrosulfide solution. The process is so hazardous and so expensive that it is now virtually obsolete.

9-27. Chemistry of Cuprammonium Rayon.—In the cuprammonium process for preparing a synthetic fiber, cotton linters are dissolved in Schweitzer's reagent, which is an ammoniacal solution of copper hydroxide that has the power of dissolving cellulose. Thus, the name *cuprammonium* has been given to identify this process. Cotton linters steeped in a mixture of ammonium hydroxide and copper sulfate go into solution, and the cellulose can be shown to exist in the form represented in Fig. 9-7. When this viscous solution is forced under pressure through a spinneret into dilute sulfuric acid or into a solution of sodium hydroxide and glucose, the cellulose coagulates into filaments that can be taken up as a thread.

9-28. Manufacturing Process.—The principle of manufacturing cuprammonium rayon is similar to that of manufacturing viscose. The cellulose is converted to a spinning form and, once spun, is regenerated to its original status by coagulating baths. The type of apparatus used for viscose spinning is used for cuprammonium-rayon spinning. An important step in the cuprammonium process is the recovery of the copper and ammonia left in solution after the cellulose coagulates. Without this recovery, the manufacture would be too costly, even though the recovery is expensive. Cuprammonium rayons can be dyed in a variety of colors.

The cuprammonium process is still in use, but the greater percentage of regenerated yarn is produced by the viscose process. Rayons are sometimes called "artificial silks," as they resemble silk in touch, durability, and beauty.

9-29. Chemistry of Cellulose-Acetate Rayons.—Cellulose-acetate rayon differs from the viscose, cuprammonium and nitrocellulose rayons. The latter three rayons are regenerated-cellulose fibers, whereas the first is an ester of cellulose. To put it another way, the yarns produced from viscose, cuprammonium, and nitrocellulose are identical in chemical composition in that the fiber is made up of a series of connected cellobiose units of pure cellulose; on the other hand, cellulose acetate is a yarn in which acetyl groups have been substituted for hydroxyl groups in the chain of cellobiose units.

A change from cellulose-acetate flake into cellulose-acetate yarn can be brought about by a purely physical process. The formation of cellulose acetate involves the bringing together of measured amounts of pure cellulose, acetic anhydride, and other ingredients, and careful watching of the ensuing process. The degree of acetylation is an important factor. Although there are variations for special-duty yarns, the proper degree of acetylation is between 54 and 55 per cent.

9-30. Manufacture of Cellulose-Acetate Rayon.—The first step in the manufacture of cellulose-acetate rayon consists in dissolving properly acetylated cellulose in acetone. The solution is then carefully filtered and put under a vacuum to remove dirt and air bubbles. A solution is forced through a spinneret and downward into a current of warm rising air, which evaporates the acetone and coagulates the fiber. The fiber, which is continuous, is wound directly on a spool, no further treatment except twisting being necessary.

Cellulose-acetate rayons can be made in a wide variety of fibers. The diameter of the holes in the spinnerets and the speed of spinning determine whether the fiber is as fine as silk or as coarse as wool. All the cellulose-acetate rayons can be dyed easily by special dye baths. The rayon can be colored directly in the spinning solution, but it has proved more economical to produce a colorless fiber and then dye it.

Cellulose-acetate rayon is available as continuous fiber and as staple fiber. Staple fiber is nothing more than standard lengths of fiber. The short lengths (1 to 6 inches long) are sold directly to the trade for weaving and spinning. Viscose fiber is also available as staple fiber.

9-31. Uses.—Cellulose acetate, besides its well-known use in clothing, hosiery, and neckwear, is used in laminated fabrics. In these applications, rayon fabric is put between two sheets of fabric, other than rayon, and the laminate is hot pressed. The rayon, being thermoplastic, softens, and the two outer fabrics firmly adhere to it. When cool, the three-piece laminate is fairly rigid and appears as a single fabric. This type of laminated fabric is widely used in wrinkleproof collars on men's shirts.

Cellulose-acetate rayons and viscose rayons behave differently toward certain dyes. A dye that affects viscose may have no effect on cellulose acetate, and a dye that affects cellulose acetate may have no effect on viscose. This peculiarity has led to the development of double dyeing. It is possible to produce many startling effects with this double-dyeing process. For example, if a cloth that contains the design of an eagle woven of viscose in a fabric of cellulose-acetate rayon is dyed in a dye bath that contains a red dye which will affect viscose but not cellulose acetate and a blue dye which will affect cellulose acetate but not viscose, a red eagle will appear on a blue background.

9-32. Future Fibers.—Ethyl cellulose is suitable for the production of fibers, but commercially none has yet made its appearance. The same may be said for acetobutyrate and many other mixed esters of cellulose. Much research work is being done on rayons to improve their physical and chemical properties. The synthetic fibers such as nylon and vinyon definitely possess some superior characteristics, which rayon research is trying to equal.

Fibers From Natural Materials

9-33. Protein Materials.—Great quantities of protein fibers are being obtained from soybeans and milk. Peanuts, cottonseed, wheat, and corn are all potential sources of protein fibers. The soybean and milk protein fibers are still in the experimental stage, although a casein fiber became commercially available in 1942.

The protein structure of molding powder has been shown by X-ray to be globular. This globular structure is caused by side reactions of the long chains. When the protein matter is used for fiber production, there must be no side chain reactions. The structure must be a simple long chain. Hydrolysis of the protein solution will usually break up any side chain reactions that might be present.

Protein fibers are thermoplastic materials of the natural resin type. The basic raw materials are any protein-bearing carriers, the two most common being soybean meal and casein. The casein is obtained by reacting milk and sulfuric acid. The soybean meal is treated with hexane or other suitable solvent to extract the oil from the meal. The residue is further extracted with a solution of sodium sulfide, and the protein matter left is finally precipitated with acid.

9-34. **Method of Manufacture.**—In general, the manufacture of soybean and casein fibers is the same. The protein matter is dissolved in sodium hydroxide. Usually a small amount of Turkey red oil or ethyl glycollate is added along with the alkali to increase the flexural strength of the end fiber. The alkali casein must ripen for about 24 hours. Hydrolysis, which occurs during the ripening period, breaks all the side chain reactions of the casein. The solution is then forced through spinnerets into a coagulating bath, the spinning process being the same as that used for rayons. There are a variety of coagulating agents that may be used. Since the casein solution is alkaline, the coagulating agent must be acid. Sulfuric and phosphoric acids are the agents most commonly used. The fibers are thoroughly washed to get rid of excess acid. As was the case with casein molding powder, the fibers must be treated to prevent moisture absorption. This treatment consists of placing them in a 5% formaldehyde bath. The fibers, being very fine, do not harden enough to render them brittle. The formaldehyde-bath treatment takes about 18 hours.

The fibers are oiled and dried, and are then wound on spools. Protein yarn is also made up as staple fiber. The yarn is usually produced in its natural color and is subsequently dyed to any desired color. Protein fibers are best compared to wool, but they are not so strong. They are considerably weaker when they are wet than when they are dry.

9-35. **Uses.**—Casein fiber is used as a substitute for wool in making felt hats and in fabrics used in upholstering and clothing. It is marketed under the name of Aralac. The fiber can be blended successfully with wool and other natural textile fibers.

9-36. **Glass.**—Glass is one of the oldest substances known to man, but fibers produced from it date back only to 1893, when fine

threads of drawn glass were used to make lace patterns. These threads were formed by drawing a heated glass rod. The fiber was drawn by revolving it around a metal drum. Glass, due to its high melting point, is an excellent substitute for asbestos. In 1938, the Owens Corning Fiberglas Corporation was formed to produce glass fiber. This corporation brought together two of the biggest names in glass, the Owens Illinois Glass Company and the Corning Glass Works.

The chemistry of glass is a study in itself. In regard to plastics, it is well to note that, while glass has all the properties of a true plastic, it is not generally referred to as a plastic material. Glass is primarily a fused mixture of white sand, soda ash, and limestone.

9-37. Method of Manufacture.—In the manufacture of glass, the correct proportions of raw materials are placed in a high-temperature oven, and the mixture is thoroughly melted. Carbon dioxide is given off in the process; so the heating must be continued long enough to remove all gas bubbles. The fused glass is then drip-poured to form marbles, each of which is inspected for air bubbles, incomplete fusion, and impurities. The perfect marbles are then placed in an electric furnace and are heated until molten. The molten glass is made to flow in a fine stream through a very small opening in a special metal that can resist high temperature, and to run onto a winding drum. The rotation of the drum draws the glass into continuous filaments. The individual filaments are then made into a single strand by another high-speed winding device. The strands are then twisted and rewound for shipment. The process may be varied to form staple fiber, which is made by drawing the glass in mat form by steam or air. The mats are formed layer upon layer and finally are cut as batting. Throughout the fibrillation process, standard textile machinery is employed. Glass fibers may be colored by incorporating coloring agents in the batch formula.

9-38. Uses.—Since glass in fiber form is soft and pliable and has none of the cutting characteristics of regular glass, it has found innumerable uses in everyday applications. Glass fibers do not sliver the finger as do fine particles of glass. Filters and insulation made from glass-fiber briquets are in common use. Drapery and upholstering fabrics of glass are becoming increasingly popular. Glass fiber is an excellent electrical insulating material.

Chapter Ten

Rubber-Like Plastics and Synthetic Rubber

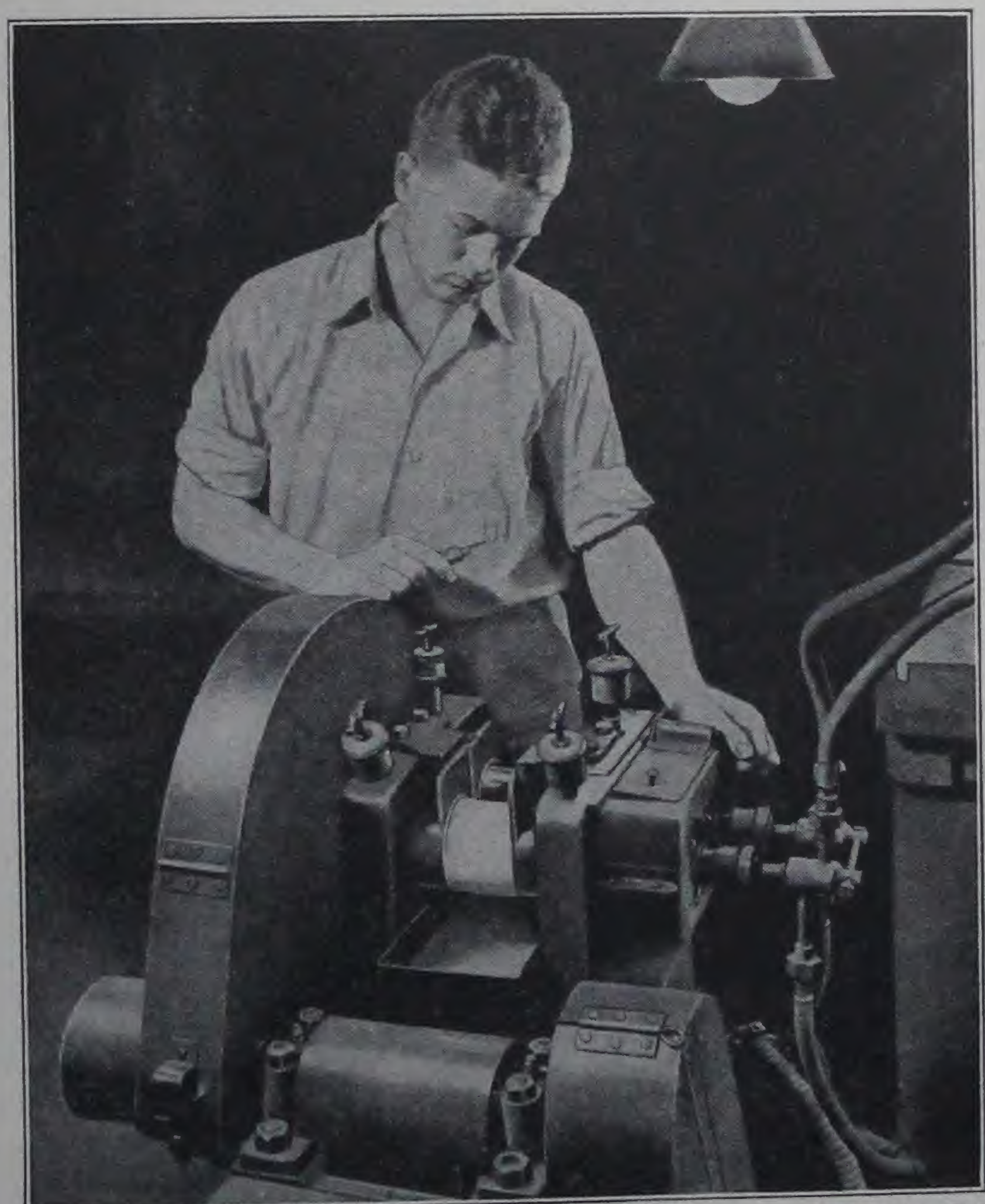
Natural Rubber

10-1. Classification of Rubber.—Rubber is divided into two general categories: natural rubber and synthetic rubber. The term *synthetic rubber* originally meant any man-made material that was indistinguishable—either physically or chemically—from natural rubber. Research has tended to prove that the physical properties of rubber are not necessarily dependent on the chemical composition of the rubber, but depend on the structure and the length of the chain making up the compound. The more recent meaning of the term *synthetic rubber*, therefore, seems to include any man-made substance that substantially approaches natural rubber in its physical properties. The word *elastomer* is sometimes used instead of the term *synthetic rubber*. Synthetic rubber is subdivided into three groups:

Simple polymers
Copolymers
Organic polysulfides

Synthetic rubber is almost always more expensive than natural rubber, but is usually superior to natural rubber in some physical or chemical characteristic. Synthetic rubber was not manufactured on a large scale until 1942, when loss of the supply of natural rubber brought about the large-scale production of synthetic rubber in the United States. Increased production has brought the price of synthetic rubber down, but the natural product is still the cheaper. Tests on the laboratory mill, shown in Fig. 10-1, were used as some of the basic controls in the synthetic-rubber development.

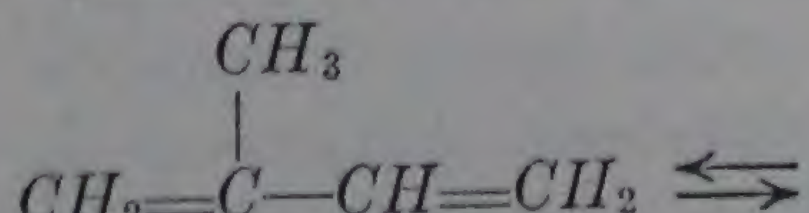
10-2. Chemistry of Natural Rubber.—In 1860 Williams obtained isoprene as a by-product of the destructive distillation of natural rubber. Others have investigated the structure of



(Courtesy of B. F. Goodrich Co.)

Fig. 10-1. Laboratory Mill Used for Synthetic-Rubber Control Tests.

rubber, and it is now believed that natural rubber is a polymer consisting of a straight chain of isoprene units, as indicated in



isoprene

natural rubber

Fig. 10-2. Structure of Natural Rubber.

Fig. 10-2. In the formula, the methyl radical, CH_3, occurs at regular intervals throughout the long chain. The exact number

of individual isoprene units comprising the rubber molecule is not known, but molecular-weight determinations indicate that it is in the thousands. Rubber, then, is a natural polymer. It should be noted that the two double bonds of isoprene break and revert outward, allowing for chain-linking. Another chemical name for isoprene is 2-methyl-1, 3-butadiene.

Attempts have been made to polymerize synthetic isoprene; but, while a rubber compound has resulted, it is not so good as the natural product. The difference might be attributed to the hap-hazard placement of the methyl radical. In natural rubber, the methyl group is always attached to every fourth carbon atom. The structure of the synthetic isoprene polymer shows irregular placement of the methyl group; sometimes it occurs at every fifth carbon atom, and sometimes at every third carbon atom.

10-3. Manufacture of Rubber.—Natural rubber is found in the tissues of rubber trees and some shrubs, from which it exudes as a milky fluid known as latex. The latex is collected in small cups placed beneath cuts made in the bark of the rubber tree. The crude latex contains a large per cent of water and impurities. When shrubs and small plants are the source of the latex, the whole shrub or plant is usually squeezed under pressure to rupture the plant cells and free the milky fluid.

After chemical purification, the crude rubber is worked on calender rolls with various softeners and fillers. The heat developed during milling causes the rubber to become plastic, in which condition it can be molded into articles. When cooled to 0° C, rubber tends to harden and assumes a crystal-like structure which stands up very poorly against the attack of many solvents, and deteriorates on exposure to sunlight, heat, and air. To increase its resistance to these agents, rubber is vulcanized. Vulcanization is a chemical reaction between sulfur, which is the vulcanizing agent, and the rubber. This reaction renders the rubber insoluble, generally. Free rubber may be reclaimed by removal of the sulfur, this removal being accomplished by boiling the rubber in a caustic-soda solution. The rubber may then be re-plasticized by adding oils and applying heat.

Simple Polymers

10-4. Neoprene.—Neoprene was developed in the United States in the laboratories of E. I. du Pont de Nemours and Company. The material is also being manufactured in other countries at the present time. The history of its development is a little vague, but 1925 is the year usually associated with its initial appearance. As a rule, neoprene is not used as a substitute for rubber, but rather it is used where natural rubber is not suitable.

The development of neoprene owes much to the work of American chemists who discovered a simple means of producing monovinylacetylene. This compound can be formed from acetylene with the aid of a catalyst, which is usually a copper-salt solution. The electric-furnace method is used to obtain acetylene from such common substances as coal and limestone. Hydrogen chloride, produced from common salt, is the other chemical used in the manufacture of neoprene. The equations in Fig. 10-3 are given to show the steps involved in the formation of neoprene. Chloroprene polymerizes to a rubber-like material more readily than does isoprene. Furthermore, the polymerization can be accomplished at room temperature in a short time. The polymerization reaction is simply a straight-chain hookup as shown by the last equation in Fig. 10-3.

$$3C + CaO \longrightarrow CaC_2 + CO$$

$$CaC_2 + H_2O \longrightarrow HC{\equiv}CH + CaO$$

$$2HC{=}CH \xrightarrow{\text{catalyst}} H{-}C{\equiv}C{-}\underset{\displaystyle H}{\underset{|}{C}}{=}\underset{\displaystyle H}{\underset{|}{C}}{-}H$$

monovinylacetylene

$$HC{\equiv}C{-}\underset{\displaystyle H}{\underset{|}{C}}{=}CH_2 + HCl \longrightarrow H{-}\underset{\displaystyle H}{\underset{|}{C}}{=}\underset{\displaystyle Cl}{\underset{|}{C}}{-}\underset{\displaystyle H}{\underset{|}{C}}{=}\underset{\displaystyle H}{\underset{|}{C}}{-}H$$

monovinylacetylene hydrogen chloride

2–chloro –1, 3–butadiene or chloroprene

$$H{-}\underset{\displaystyle H}{\underset{|}{C}}{=}\underset{\displaystyle Cl}{\underset{|}{C}}{-}\underset{\displaystyle H}{\underset{|}{C}}{=}\underset{\displaystyle H}{\underset{|}{C}}{-}H \longrightarrow -\underset{\displaystyle H}{\underset{|}{C}}{-}C{=}C{-}\underset{\displaystyle H}{\underset{|}{C}}{-}\underset{\displaystyle H}{\underset{|}{C}}{-}C{=}C{-}\underset{\displaystyle H}{\underset{|}{C}}{-}$$

chloroprene → neoprene

Fig. 10-3. Formation of Neoprene.

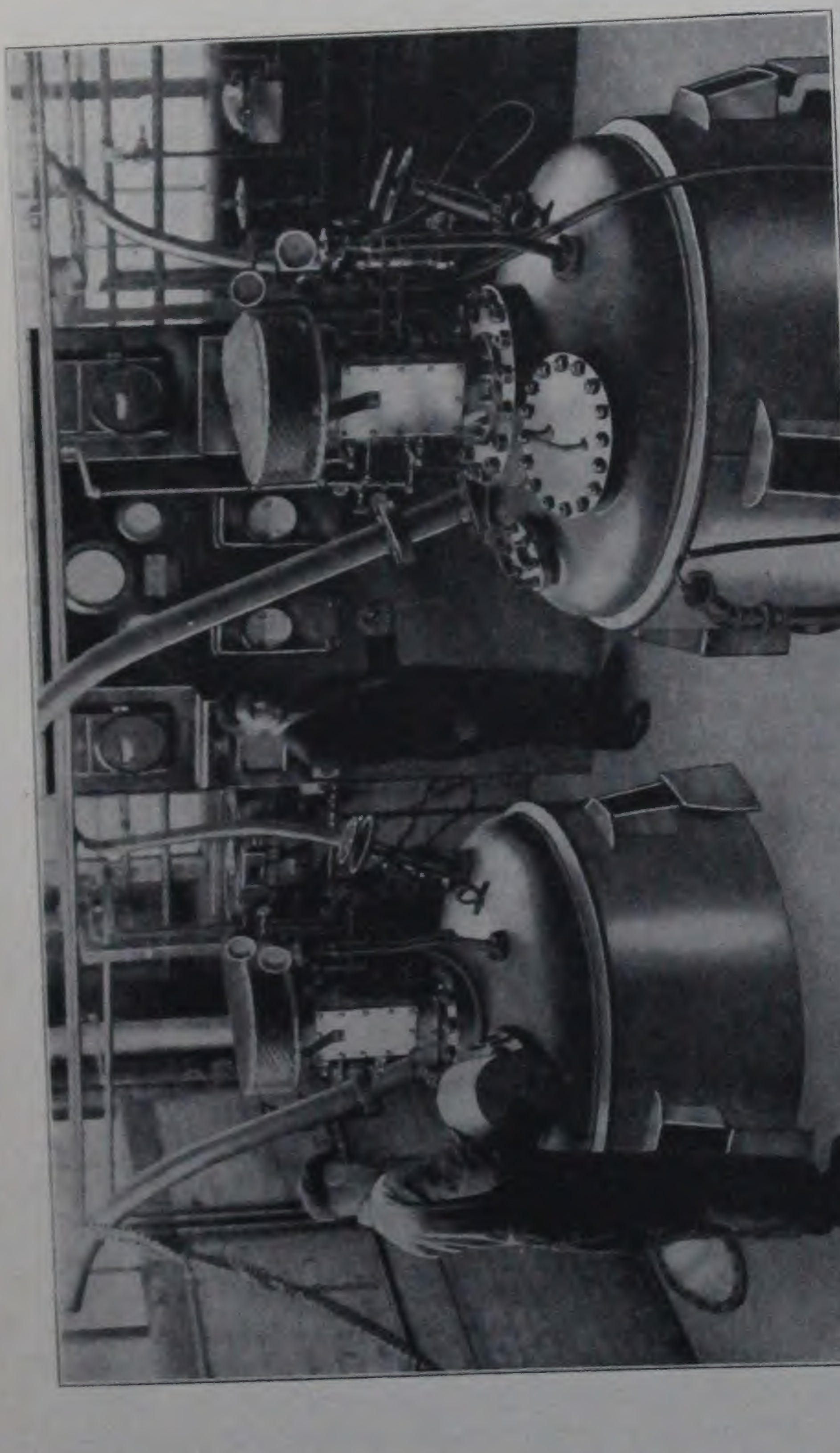


Fig. 10-4. Reaction Kettles for Formation of Chloroprene Monomer. (Courtesy of B. F. Goodrich Co.)

10-5. Raw Materials.—Neoprene is a thermosetting type rubber of the synthetic-resin variety. The basic raw material is acetylene, which is prepared from coke and lime. Sulfur is not needed as a vulcanizing agent, but various other modifiers have been used. Magnesia has been used for increasing the strength of the rubber and as a neutralizer for any hydrochloric acid that may be liberated in the vulcanizing process. Zinc oxide is sometimes used to speed up, or accelerate, the cure of neoprene. Litharge (lead oxide) is used to give the neoprene compound increased water resistance.

10-6. Manufacture of Neoprene.—Neoprene production consists of two steps. The preparation of the monomer and the subsequent polymerization comprise the first step. The second step involves the compounding of the polymer with coloring and modifying agents. The chloroprene monomer is formed in an ordinary reaction kettle, as shown in Fig. 10-4. The various factors that control the polymerization, such as temperature and pressure, are regulated by means of the controls on the instrument panel in the background. The polymerization process is slightly different from that used for ordinary resins; the emulsion-polymerization method, similar to the one used in the production of acrylic plastics, is applied. Chloroprene is readily emulsified in water by soap or by any synthetic emulsifying agent. During the polymerization, hydrochloric acid is usually liberated, and, for this reason, ammonia must be added to prevent the acid from precipitating the polymer. Beta-naphthylamine is added to the mixture as a stabilizing agent.

The emulsion polymerizes evenly and rapidly into a hard polymer, which, when dry, is ready for processing. Neoprene is a versatile resin that may be used with a wide variety of materials to produce compounds possessing various physical and chemical properties. The compounding of neoprene is done on standard rubber-working machinery. The use of carbon black makes a harder compound but does not increase the tensile strength.

When the rubber is incorporated in the pores of a fabric to be used as tire cords or as balloon fabric, a three-roll calender is used. The calender consists of three horizontal rolls set one above the other. The neoprene is fed between the top and middle rolls, and the fabric between the bottom and middle rolls. The neoprene,

which coats the middle roll, is ground into the fabric. A spreading process is sometimes employed to obtain the same effect. This process consists in dissolving the monomer and the vulcanizer in a solvent, such as gasoline, and spreading the mixture over the cloth.

Once the article has been formed, it must be vulcanized. With neoprene, sulfur is not necessarily the vulcanizing agent, although the term *vulcanizing* is still used. The vulcanizing agent depends on the material being vulcanized.

10-7. Properties of Neoprene.—Neoprene is manufactured in some countries under the trade names of Sovprene and Mustone. Its properties may be considered as representative of all synthetic rubbers of the chlorobutadiene type. Table 10-1 gives a general idea of how neoprene compares with natural rubber in its behavior toward common solvents in the unvulcanized stage.

TABLE 10-1

SWELLING OF NEOPRENE AND NATURAL RUBBER

(Sample immersed in liquid for 8 weeks at 20° C)

Immersion Liquid	Per Cent of Volume Increase	
	Neoprene	Natural Rubber
Benzine	0	160
Gasoline	8	230
Carbon tetrachloride	160	670
Acetone	25	0
Transformer oil	0	150
Turpentine	90	300
Benzene	160	370

Neoprene is resistant to solutions of salts, acids, and alkalies, but is attacked by some oxidizing acids. Ozone has no effect on neoprene. Neoprene has an excellent resistance to "sun checking," or the cracking, or crazing, of rubber caused by exposure to sunlight. Sunlight is probably the most destructive agent of natural or synthetic rubber.

When all the physical properties are taken into account, rubber is superior to neoprene. Comparisons of elongation and tensile-strength values are difficult because of the variety of compounds. There are many types of neoprene made for specific jobs.

Published figures on the tensile strength of neoprene range from 200 to 4,000 pounds per square inch. In general, the elongation and tensile strength of natural rubber exceed those of neoprene.

10-8. Uses.—Its excellent oil and gas resistance make neoprene useful as fuel-oil and gasoline-pump hose. Rubber that is used in connection with oil or gasoline is being replaced by neoprene. Printing rollers are now made from chlorobutadiene materials, owing to the stability of the material when in contact with printing inks and washes. Neoprene is being used for protective clothing such as heavy-duty raincoats and sportsmen's jackets. The insulation of cable which must withstand all kinds of weather is made of neoprene.

10-9. Butadiene Polymers.—The butadiene rubbers, which are both simple polymers and copolymers of butadiene, are generally referred to as Buna rubbers. The name Buna is derived from the first two letters of the words *butadiene* and *natrium*. Natrium is the Greek word for sodium, the element that has the ability of polymerizing butadiene. It was known as early as 1892 that the higher homologs of butadiene would polymerize to form rubbery substances. Butadiene at normal temperatures is a toxic, highly reactive gas that was first polymerized by Russian chemists in 1910. This important contribution to science created the desire to produce synthetic rubbers to compete with the natural product.

The problem at hand was to find a cheap and abundant source of butadiene. Three independent groups of chemists in three different countries produced butadiene synthetically. The methods were all different, but all three proved expensive and impractical. The Buna rubber situation remained stagnant until 1927, when a method of synthesizing butadiene from acetylene was discovered. Butadiene is produced by catalytic dehydrogenation of butenes and butanes from gas and petroleum, but the destructive distillation of ethyl alcohol from the fermentation of grains, potatoes, and sugar to produce butadiene is gaining favor in an effort to conserve petroleum resources.

The Buna rubbers are polymerization products. The trade names are characterized as Buna 85 or Buna 115, the numbers indicating the average molecular weights in thousands, as 85,000 and 115,000, respectively. The polymerization is shown by the following equation:

$$\underset{\text{butadiene}}{CH_2{=}CH{-}CH{=}CH_2} \xrightarrow{\text{catalyst}} \underset{\text{Buna rubber}}{(-CH_2{-}CH{=}CH{-}CH_2-)_x}$$

It is a typical rubber polymerization, in which the two double bonds break and revert outward to permit formation of the chain. The only difference between natural rubber and the simple butadiene polymers is the methyl group on the second carbon atom in the natural-rubber structure, where the butadiene has a hydrogen atom instead of a methyl group.

10-10. Method of Manufacture.—The conversion of butadiene from monomer to polymer may be accomplished in either of two ways. Sodium may be used as a catalyst for regular heat polymerization, or the monomer may be suspended in water and a heat-emulsion polymerization used. The latter method is preferable, since the reaction proceeds evenly and may be kept under better control. The duration and temperature of the polymerization reaction control the type and length of the chain compound formed. The compounds, when X-rayed under tension, all show a fiber structure, which leads to the theory that the polymerization is a linear one and the side linkages (reactions perpendicular to the long straight chain) are at a minimum.

All Buna rubbers of the simple-polymer type must be vulcanized. This process, in which sulfur is used as the vulcanizing agent, renders the compound thermosetting. The amount of sulfur will control the rigidity of the final product. In this respect, the Buna compounds are like natural rubber and unlike Neoprene. If enough sulfur is used, a hard-rubber compound resembling ebonite is formed. Zinc oxide and lampblack can be compounded with the polymer to produce special-duty rubbers.

The simple polymers of butadiene have been supplanted to a large extent by the copolymers, which have a wider range of properties because of the numerous compounds that are compatible with butadiene. Simple Buna polymers are marketed under such names as Buna 85, Buna 115, SKB, SKA, and Ker.

10-11. Isobutylene Rubber.—Rubber from isobutylene was first discovered in Germany, where it was marketed under the name *Oppanol*. Research by an American oil company produced a similar but better material, which is called *Vistanex*. On account of their peculiar chemical linkage, the isobutylene polymers are

sometimes not thought of as rubber compounds. Their physical properties, however, are close enough to those of natural rubber to include them in a discussion of rubber.

Isobutylene is a by-product of the thermal cracking of petroleum, and it is a gas at normal temperature. The monomer polymerizes end-to-end in the regular fashion, as shown in Fig.

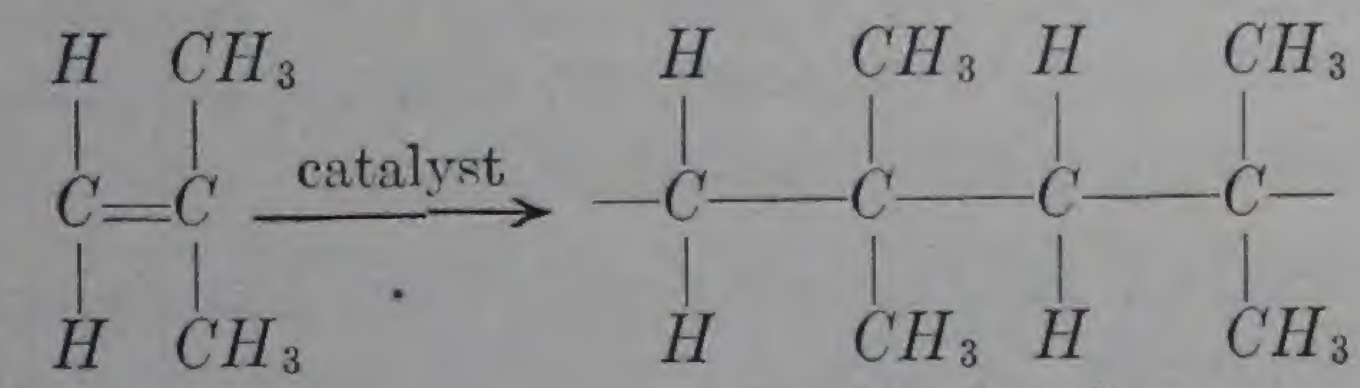


Fig. 10-5. Polymerization of Isobutylene.

10-5. The molecular weight of the commercial polymer is about 100,000, which means that about 1,800 units are linked together. It should be noted that the finished polymer does not contain double bonds. Since vulcanization is believed to be related to the chemical unsaturation of a compound, this fact perhaps explains why isobutylene cannot be vulcanized. Isobutylene polymers are completely saturated.

10-12. Manufacture of Polymer.—Monomeric isobutylene is polymerized at low temperatures by using boron trifluoride as the catalyst. The reaction is extremely rapid and, for that reason, the concentration of the catalyst and the polymerizing temperature must be carefully checked. Other catalysts, such as iron and titanium dioxide, have been used, but the results were not so satisfactory. The temperatures needed to produce high molecular compounds are quite low. A molecular weight of 100,000 necessitates a temperature of −85° C. The polymerization reaction is exothermic, and it is necessary to remove the heat evolved as fast as it is formed.

Polyisobutylenes are unstable to prolonged heating periods, so that the temperature of the rolling operation must be kept below 110° C to prevent chemical decomposition. Sulfur is a good stabilizer and greatly lessens the danger of the polymer reverting to its monomeric form (depolymerization). The material is milled on standard rubber-working equipment. Crude isobutylene is almost pure white in color. Various fillers and coloring agents are

added during the rolling process to improve the properties of the finished compound.

10-13. Properties and Applications.—Isobutylene rubbers are extremely resistant to strong mineral and oxidizing acids. Vistanex is soluble in most hydrocarbon solvents, but it shows good resistance to ketones and alcohols. It is not affected by ozone. The material is superior to natural rubber in moisture resistance, but it is inferior in tensile strength. The latter drawback limits the use of Vistanex. It is generally used as a modifier of other rubber compounds.

A well-dispersed mixture of natural rubber and Vistanex produces a material that is superior to natural rubber. Vistanex is compatible with asphalt and other natural resins. Asphalt-Vistanex and rosin-Vistanex mixtures can be used where natural rubber cannot be used.

Its impermeability to gases makes Vistanex suitable for gas-proofing cloth and for balloon housings. Low-molecular polymers are used in lubricating oils and greases to decrease the tendency of the oil or grease to thicken at low temperatures. Many of the so-called hard-rubber battery cases are made from high-molecular, filled polymers of isobutylene.

10-14. Polyvinyl-Chloride Rubbers.—Polyvinyl chloride has already been mentioned as a molding compound. The heavily plasticized compounds are similar in properties to rubber and are usually regarded as synthetic rubbers. The plasticized compounds are thermoplastic. The chemistry is the same as for the vinyl-chloride molding compounds. It is interesting to note that polymerized vinyl chloride, the structure of which is shown in

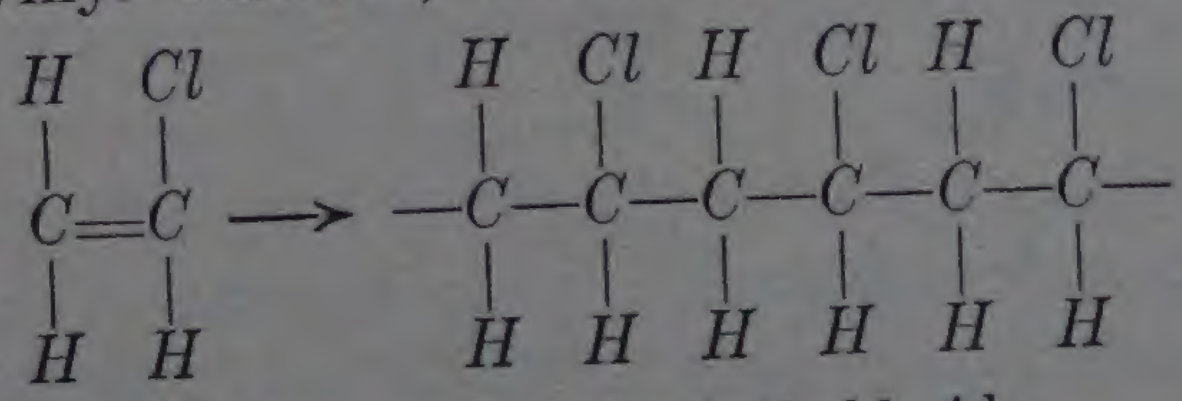


Fig. 10-6. Polymerization of Vinyl Chloride.

Fig. 10-6, has no double bonds. The rubber-like compounds therefore cannot be vulcanized. Attempts have been made to add thermosetting resins to polyvinyl chloride. The heat treatment does set up the resin and, since the chloride is homogeneously

mixed with it, it appears to be vulcanized. In the true sense of the word, no vulcanization actually takes place.

10-15. Plasticization of Polymer.—The polymer of vinyl chloride is plasticized and colored in a blender or mixer. When the "dough" stage is reached, the mass is placed on regular rubber mills. The batch soon smooths out and an even mixture results. A variety of plasticizers are in use, but the two most common ones are tricresyl phosphate and dioctyl phthalate. When from 40 to 50 per cent of plasticizer is used, the maximum values for hardness and tensile strength are obtained. By varying the amount and type of plasticizer, different kinds of rubbers are obtained. Nonetheless, control of the molecular weight of the polymer is also very important. Polyvinyl chloride is one of the few plastics that have a "point-to-point" value with a plasticizer. For example, the properties of a high-molecular-weight polymer with 50 per cent of plasticizer will be almost identical with those of a low-molecular polymer with 20 per cent of plasticizer. The only difference between the two compounds is that one is more flexible than the other, and, surprisingly, the one with the higher amount of plasticizer is the harder of the two. The type and amount of plasticizer to be used depend almost wholly on the ultimate use of the compound.

Since hydrogen chloride is one of the basic materials used in making polyvinyl chloride, high working temperatures liberate the gas. Certain lead and calcium salts, if present in small amounts, tend to stabilize the polymerized compound and to retard decomposition at high temperatures. Inasmuch as the lead and calcium salts are acted upon by the hydrogen chloride that is liberated, an inactive salt filler is the net result. The small amount of stabilizer used does not seem to affect the electrical characteristics of the polymerized product.

Owing to the high plasticizer content, the milling temperatures of polyvinyl-chloride rubber are lower than those for most other materials. Temperatures ranging from 280° to 300° F are sufficient.

10-16. Properties and Applications.—Highly plasticized stock of polyvinyl-chloride rubber is suitable for extrusion and injection molding. This same material may be calendered with roll fabric to produce impregnated cloth. Polyvinyl chloride in solution is an excellent coating material. In certain cases, the polymer is milled with as high as 150 per cent of its weight of plasticizer. This pro-

portion produces a jelly-like solution that is used for making flexible molds for casting plaster.

Polyvinyl chloride has excellent flexural strength. In this respect, it is better than natural rubber. It is used to advantage in the shoe industry for soles and heels. It is made into gaskets and tubing to be used where oil resistance is demanded in a rubber-like compound. Bumper pads and diaphragms for the automobile and aircraft industries use large amounts of this type of synthetic rubber. Polyvinyl chlorides will find use wherever there is a possibility of corrosion. These products are known by such names as Koroseal, Flamenol, Vinylite, Korogel, and Korolac.

10-17. Polyethylene.—The idea of a polymerized ethylene material started with Imperial Chemical Industries, Ltd., of England several years before World War II. This company showed great foresight in realizing that England imported all her rubber and that, without rubber, many of the modern communication instruments could not be made. Soon after the invasion of Poland by Germany, a pilot plant was constructed; and the disaster at Dunkirk and the success of the pilot plant led to the inauguration of the first production plant. It is hardly enough to state that polyethylene proved a giant in Great Britain's war effort.

Since much scientific development was shared by the Allies during the war period, it was only natural that the United States should produce the original substance in volume and further develop it. Led by the research of DuPont and Union Carbide and Carbon, experiments were [illegible]. As a result, this new material is now available to the plastics industry.

Polyethylene, or polythene as it is more commonly called, is a thermoplastic material of the synthetic resin variety. It is simply ethylene that is polymerized according to the formula represented in Fig. 10-7. Although a whole series of polythene compounds may be obtained, the name polythene applies only to those solid polymers that are suitable for use in molded plastics.

Under controlled conditions of temperature and pressure, the liquid ethylene obtained from natural gas or cracked petroleum hydrocarbons polymerizes to form a straight-chain polymer of ethylene. X-ray study shows that polythene constitutes a series of four grouped CH_2 radicals. The structure is peculiar in that it is not 100 per cent crystalline. Examination of changes in physical

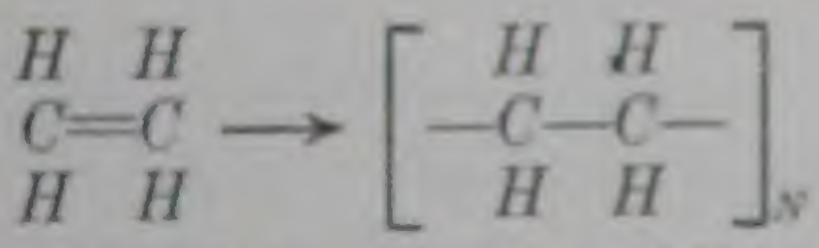


Fig. 10-7. Polymerization of Ethylene.

properties with variations in temperature definitely indicates the presence of the amorphous state. The ratio of crystalline material to amorphous material will vary with the molecular weight of the polythene; and the melting or softening point also depends on the molecular weight. Polythene, like all crystalline materials, has a well defined melting point.

Unplasticized polythene possesses some excellent properties, but more and more commercial uses require plasticizer and coloring matter. The polymer formed by regular application of confined heat and pressure may be further processed by calendering or by mastication. The granules are fibrous and, for ease of handling and molding, they are sometimes cut into cubes.

Polythene is used for coatings, as well as for molded articles. Solvents and diluents must be added to the material to produce suitable spray coatings. A large variety of solvents and resins for augmenting certain properties are available.

10-18. Properties of Polythene.—Long exposure of polythene leads to the impairment of some of its best properties. In order to counteract this deterioration, an anti-oxidant is added. The amount used is so small that the anti-oxidant does not have an appreciable effect on any of the other properties. It has been proved also that a small amount of anti-oxidant is effective for a very long time.

Polythene may be made either rigid or flexible, the degree of stiffness depending on the formula and the molecular weight. This means that the material is available as film and foil and also as sheets, rods, and tubes. Polythene is extremely light in weight, having a specific gravity of only .92, which is considerably lower than that of most other plastics. This property should make the use of the material economical. Also, since polythene floats in water, the construction of floats and other aquatic articles made from an unsinkable plastic is an actual possibility.

Polythene has a tensile strength of 1,900 pounds per square inch. It offers excellent resistance to the passage of electric current and absorbs little water, and it is therefore almost ideal for use in high-frequency cables. The coefficient of thermal expansion is

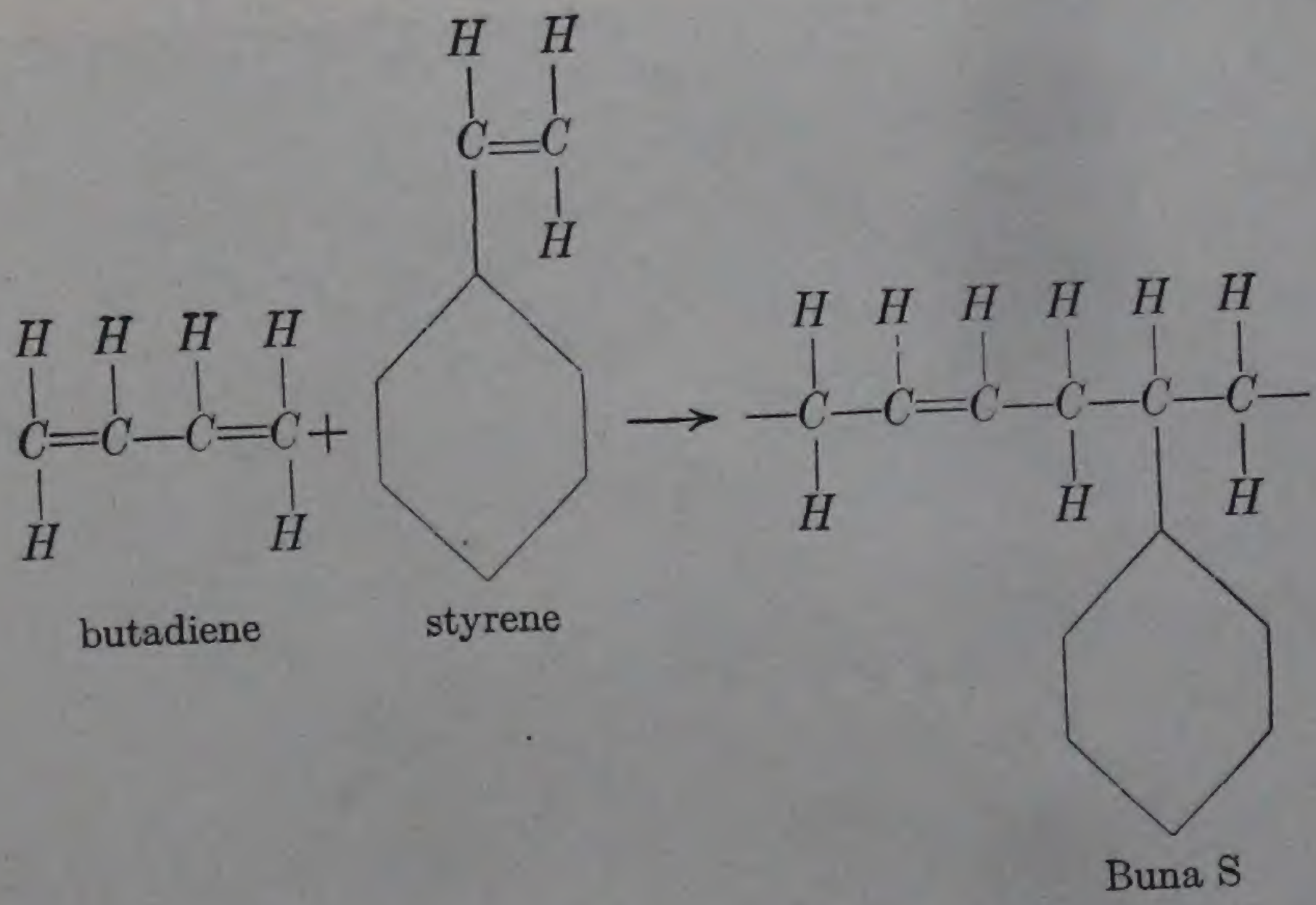


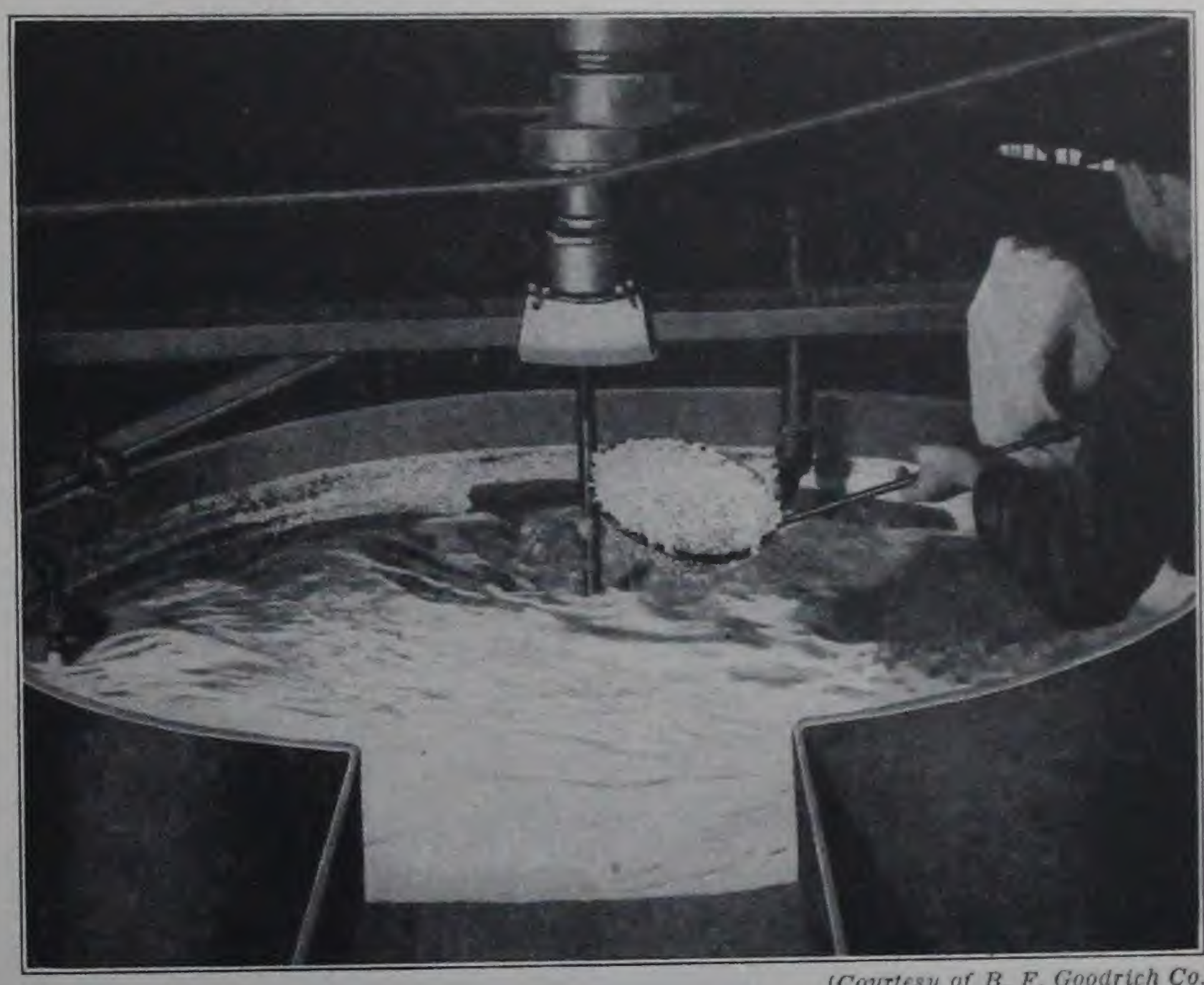
Fig. 10-8. Formation of Buna S.

very high, however, and thick sections should be avoided. Moreover, shrinkage is a bad feature where inserts or cores would be needed. It is almost impossible to mold polythene around a metal core and obtain an electrical seal (an insulation free from air voids or leaks) because the plastic material pulls away from the metal core.

10-19. Applications and Names.—Polythene and Polyethylene are the names under which the material is marketed in the United States. In Great Britain it is known as Alkathene. The material is suitable for extrusion and for compression and injection molding. It is also produced as continuous threads and foils for the packaging and textile trades. Probably its greatest individual use is for high-frequency cable. Because of its nature, it is a specialized material and will not be used for notions and novelties. As further developments are made, it will no doubt take its place with the other thermoplastic materials.

Copolymer Rubbers

10-20. Buna S.—Buna S, or Buna SS, is a copolymerization product of butadiene and styrene. The reaction that forms Buna S, which is typical of a molecular chain formation, is shown in Fig. 10-8. The copolymer is highly saturated, only one double bond



(*Courtesy of B. F. Goodrich Co.*)

Fig. 10-9. Strainer Full of Synthetic Rubber Particles Removed From Solution in Vat.

occurring at every sixth carbon atom in the straight chain. The mechanism of polymerization is the same in both Buna compounds. The double bonds break and revert outward, and by this phenomenon a chain is built up. The proportions of butadiene and styrene may be varied, although a tire rubber is being produced by mixing 3 parts of butadiene and 1 part of styrene. While the exact chemical structure of the copolymer is not certain, it is known that cross-linking of the polymer chain does occur. Molecular-weight concentrations play an important part in the structure of the final copolymer.

10-21. Method of Manufacture.—The emulsion-polymerization method is used to produce the copolymer. Both styrene and butadiene monomer are made to react in a solution of soapy water. Almost any oleate or palmitate soap may be used as an emulsifier. A catalyst such as hydrogen peroxide accelerates the polymerizing reaction. After the proper amount of chemical reaction has taken place, a stabilizer is added to halt the uniting process. Egg albumen, starch, blood serum, and glue are effective stabilizers. At the end

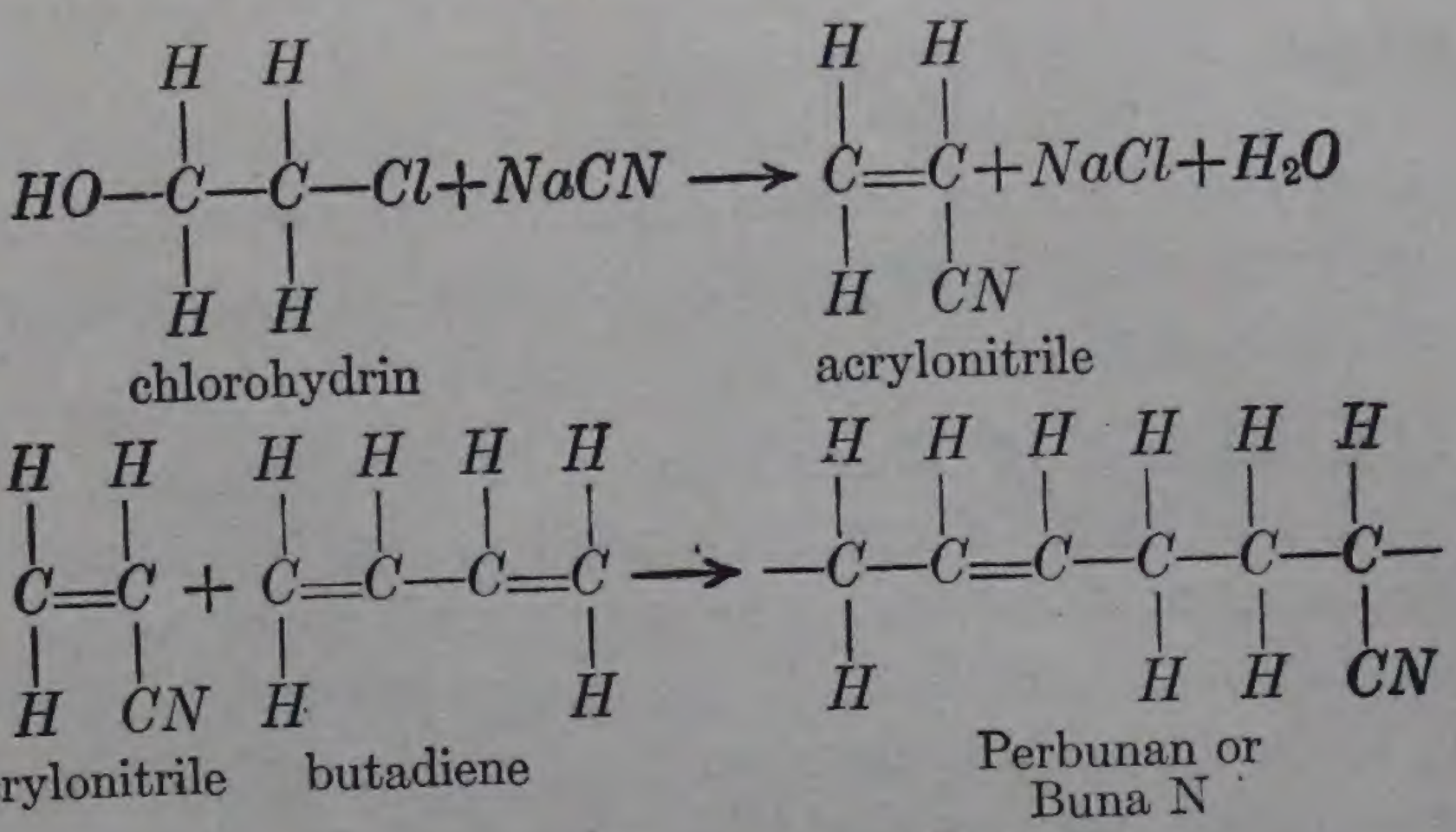


Fig. 10-10. Formation of Perbunan.

of the reaction the mixture is like natural-rubber latex. By adding a salt solution that contains sulfuric acid, the liquid latex is congealed into small particles of rubber. The rubber particles, or Buna-S crumbs, are washed thoroughly and dried preparatory to milling. A strainer full of rubber particles from the vat in which they are being washed is shown in Fig. 10-9.

Sulfur is used in the vulcanizing process, which renders the compound thermosetting. Carbon black is added during the milling operation to increase tensile strength, and an anti-oxidant is generally milled into the rubber to preserve it.

10-22. Properties and Uses.—Buna S is superior to natural rubber in its resistance to heat and abrasion, and in its electrical properties. Since it consists entirely of hydrocarbons, it is subject to swelling by oils and certain solvents. Buna S is more stable when exposed to sunlight, and has a lower moisture absorption, than natural rubber. It is compatible with natural rubber, with which it may be mixed in almost any proportion. The largest consumption of Buna S will be in the manufacture of automobile tires. A considerable amount of retreading can be done with synthetic rubber of the Buna-S variety. Buna S is used in large amounts for insulation on wire cables. In some cases, where it is desirable to protect natural rubber from the weather, Buna S is applied as a protective coating.

10-23. Perbunan.—Perbunan is a copolymerization product of butadiene and acrylonitrile (vinyl cyanide). Acrylonitrile is prepared from chlorohydrin, $CH_2Cl \cdot CH_2OH$, and sodium cyanide, $NaCN$. The reactions are shown in Fig. 10-10. The copolymeriza-

tion reaction of Perbunan is similar to that of Buna S. Also, the saturation is approximately the same in that the chain contains one double bond per six carbon atoms. The presence of nitrogen in the polymer chain is responsible for some of the superior properties of Perbunan.

10-24. Method of Manufacture.—The monomers of butadiene and acrylonitrile are suspended in an emulsion, and a peroxide catalyst is added. The compound copolymerizes to a latex similar to that of Buna S. The mixture consists of approximately $1\frac{1}{2}$ parts of butadiene to 1 part of acrylonitrile. When copolymerization has reached the proper stage, the reaction is arrested and the product is precipitated. It is thoroughly washed and dried. Perbunan is harder than Buna S or natural rubber, and it is necessary to use a softening agent with it in the milling process. Esters, such as dibutyl phthalate, are usually employed, although stearic wax and petroleum oils work satisfactorily. The addition of carbon black greatly increases the tensile strength of Perbunan.

Perbunan is vulcanizable. Sulfur is the agent used, but smaller amounts are required than those employed for natural rubber. The vulcanization process changes the Perbunan from a thermoplastic to a thermosetting compound. To prevent further polymerization on standing, a stabilizer or inhibitor, such as beta-naphthylamine, is added. Carbon black is not used when Perbunan is made as a white compound; so the tensile strength of such a compound is lower than that of Perbunan that contains carbon black.

10-25. Properties and Applications.—The chemical properties of Perbunan are governed by the acrylonitrile content of the product. The higher the content, the better the chemical resistance. The limit of the nitrile content is that amount of nitrile that starts to decrease materially the tensile and mechanical strength. Perbunan is a good heat-resistant and abrasion-resistant material, but is at its best in solvent resistance. Table 10-2 illustrates this property by comparing Neoprene with Perbunan. Perbunan Extra is the premium compound which contains a higher concentration of nitrile than the regular Perbunan.

In general, the Perbunan compounds are tougher and drier than natural rubber. For this reason, the milling operations are more difficult than for Buna S or natural rubber. The Perbunans

are more expensive than the Bunas, mainly because of the cost of acrylonitrile.

Perbunan compounds, known as American rubbers, are marketed under various trade names, such as Hycar and Chemigum. They are widely used as a substitute for the natural product and in some instances where the natural product fails. Tires have

TABLE 10-2

SWELLING OF NEOPRENE AND PERBUNAN EXTRA

(Sample immersed in liquid for 8 weeks at 20° C)

Liquid Immersed in	Per Cent of Volume Increase	
	Neoprene	Perbunan Extra
Benzine	0	20
Gasoline	8	0
Kerosene	60	0
Fuel oil	0	0
Transformer oil	0	0
Acetone	25	100
Benzene	160	140
Turpentine	90	30

been made from Perbunan, but, in general, the compounds are used in applications that require resistance against solvent liquids. Belts, gaskets, tubing, and diaphragms are a few of the many uses of Perbunan.

10-26. Butyl Rubber.—Butyl rubber is a copolymer of isobutylene and butadiene or isoprene. Although isobutylene cannot be vulcanized, the addition of butadiene or isoprene produces an unsaturated product known as Butyl rubber which can be vulcanized. Butyl rubber consists mostly of isobutylene, from 2 to 5 per cent of a diolefin being mixed with it. The product therefore has low saturation and resembles natural rubber in appearance.

Butyl rubber is an outgrowth of work done with Vistanex. While the exact manufacturing methods are a trade secret, it is assumed that a low temperature polymerization is employed. Pigments and modifying agents can be added to Butyl rubber, which is worked on standard rubber-working machinery.

10-27. Properties and Applications.—Butyl rubber has excellent electrical properties and shows no deterioration on exposure to ozone. Its resistance to solvents is not so good as that of Neoprene or Perbunan Extra, but it has good resistance to concentrated acids and metallic salts. The mechanical strength of Butyl rubber is not so great as that of the natural product. The material ages more rapidly than the natural product, but it retains its chemical resistance longer. Butyl rubber will swell in oil, but its resistance to oil is superior to that of natural rubber. It also has good resistance to water absorption and to gas permeation.

Butyl rubber is being developed to improve many of its defects. Although automobile tires have been made from Butyl rubber, they are inferior to those made of natural rubber. Laboratory tubing and gas-resistant cloth are made of Butyl rubber. With further research, Butyl rubber may become one of our most important synthetic rubbers.

Organic Polysulfides

10-28. Chemistry.—Of the synthetic rubbers, the polysulfide rubbers bear the least resemblance to natural rubber as far as chemical structure is concerned. These materials were accidentally discovered in 1920 by J. C. Patrick, an American chemist, who obtained a rubbery product from the reaction between ethylene dichloride and sodium polysulfide. Unlike other synthetic rubbers, the polysulfides are a condensation product of a chemical reaction. The usefulness and applicability of these products are noteworthy, since it is reported that many countries besides the United States have set up manufacturing facilities to produce related materials. They are marketed in the United States in various grades, as Thiokol A, Thiokol B, etc.

The substances used in the formation of organic polysulfides are a hydrocarbon dihalide, such as ethylene dichloride, and a polysulfide solution. Natural gas and refinery hydrocarbons yield dihalides, or halogen-substituted compounds, upon halogenation (a reaction involving chlorine, bromine, or iodine). The polysulfide most used is sodium tetrasulfide, Na_2S_4, which is obtained by reacting sodium hydroxide in solution with sulfur.

The chemical reactions involved in the preparation of Thiokol A and Thiokol B are as shown in Fig. 10-11. In each reaction two

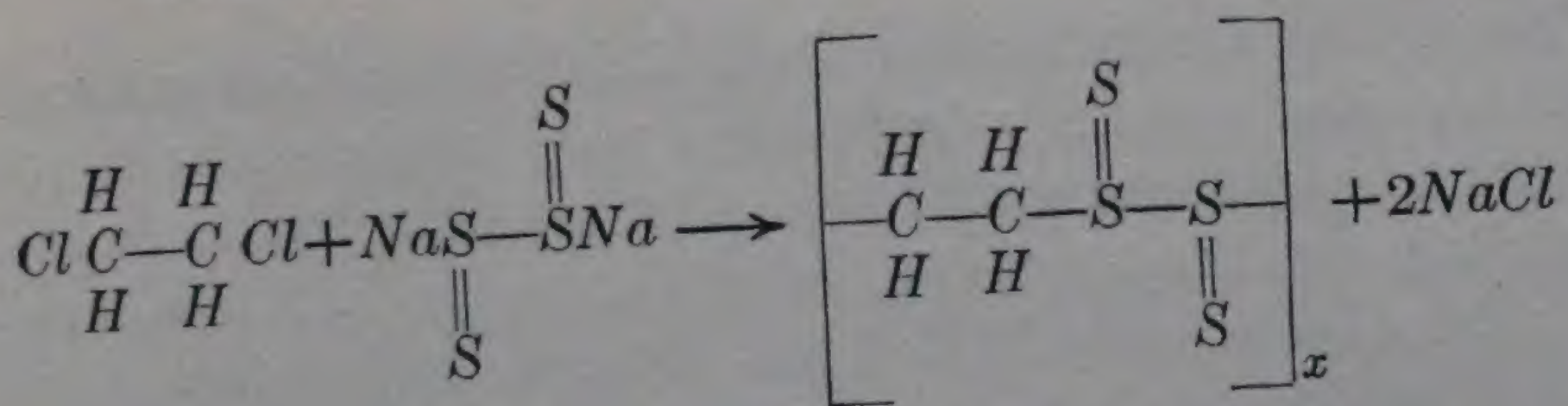


Fig. 10-11. Formation of Thiokols.

atoms of sulfur become part of the chain structure, while the other two are attached as side linkages. The two atoms which are side-linked may be removed by treatment with sodium hydroxide. However, the resulting product does not exhibit the characteristics of rubber. As a general statement, it can be said that no less than four atoms of sulfur should be contained in a unit of the final product for it to be a synthetic rubber.

10-29. Method of Manufacture.—Thiokol is produced for use not only as a synthetic rubber but also as a molding compound. The condensation polymer is thermoplastic after processing, provided it is not vulcanized. In the transformation of Thiokol into synthetic rubber, the process of vulcanization results in a thermosetting material. The chemical reaction between the initial substances is so exothermic that extreme care must be taken to see that the temperatures are kept below a certain explosive limit. The purity of the reacting materials affects the quality of the product being formed. The sodium chloride formed in the condensation reaction is drawn off in solution.

For use as a synthetic rubber, Thiokol must be vulcanized. Metallic oxides are the vulcanizing agents, while sulfur is sometimes used as an accelerator. Fillers such as carbon black are added to help increase the tensile strength of the rubber. The vulcanization of Thiokol is entirely different from that of natural rubber. It is believed that the oxidation which takes place during the vulcanizing process causes cross-linking of the chains. Thiokol may be copolymerized by employing two different dichlorides in the initial condensation reaction. The condensation of the two different compounds with the polysulfide takes place, with the formation of an interlinking chain.

Thiokol molding powders do not contain metallic oxides or vulcanizing agents, but pigments and fillers may be used. At the present time, not much use has been made of the molding compound, since the molding of flexible articles is fairly recent.

Thiokol has an objectionable odor, which is caused by a mercaptan formation at the end of the polymer chain. The chemical structure of the mercaptans, which are usually bad-smelling, is represented by the formula $R—S—H$, in which R may be an alkyl or aryl group. When the polymer is precipitated by acids, the mercaptan structure is formed. Much has been done to neutralize the odor of Thiokol, but the results have not been completely successful.

10-30. Properties.—The notable property possessed by Thiokol is its solvent resistance. Table 10-3 compares Thiokol A with natural rubber as to the action of various solvents on each. Benzene appears to be the only solvent that has any effect on Thiokol. In general, the proper Thiokol can be found that will be resistant to aromatic and chlorinated hydrocarbons, alcohols, ketones, and esters. In contrast with their excellent solvent resistance, polysulfide rubbers do not possess as good mechanical properties, such as strength, abrasion, and tear resistance, as the natural product. These materials have a tendency toward cold flow. This tendency is somewhat decreased by the addition of fillers or by compounding with other synthetic or natural rubbers. Polysulfides possess good electrical properties. Sunlight and ozone have no effect on these synthetics, and their age resistance is excellent.

10-31. Uses.—Polysulfides can be used in practically all applications where synthetic rubber is employed. It is only natural

(Courtesy of B. F. Goodrich Co.)

Fig. 10-12. Synthetic Rubber Tractor Tire About to Be Removed From Mold.

TABLE 10-3

COMPARATIVE SWELLING OF THIOKOL A AND NATURAL RUBBER

(Sample immersed in liquid for 8 weeks at 20° C)

Liquid Immersed in	Per Cent of Volume Increase	
	Thiokol A	Natural Rubber
Light oil	0	160
Gasoline	0	230
Benzene	7	370
Carbon tetrachloride	0	670
Turpentine	0	300

that the excellent solvent resistance of these materials should lead to uses where contact with solvents is a primary consideration. Thiokol hoses for paint-spray, gasoline, and oil are in great demand. For other applications the polysulfide rubbers are available as

hot-spray powders. The process of spraying makes possible the coating of metals and other surfaces with an elastic film that possesses excellent solvent and moisture resistance. Formerly polysulfide rubbers could be used only in recapping and retreading automobile tires, but the complete tire can now be fabricated by the use of specially prepared polysulfide copolymers.

Miscellaneous Synthetic Rubbers

10-32. Ameripol.—Ameripol is a butadiene copolymer patented and manufactured exclusively by the B. F. Goodrich Co. In 1940, the Goodrich Company placed on the market, for the first time, passenger-car tires made of Ameripol. Their synthetic material is useful in applications common to other synthetic rubbers. Currently, Ameripol is produced in a variety of formulas for general and special purposes. The tractor tires about to be removed from the molds shown in Fig. 10-12 were fabricated of Ameripol.

10-33. Tornesit.—Produced exclusively by the Hercules Powder Company, tornesit is a product obtained by chlorinating natural rubber. Natural rubber apparently contains one methyl group and seven hydrogen atoms for every four carbon atoms in the polymer chain. The chlorination substitutes four chlorine atoms for four hydrogen atoms, and it is believed that one carbon atom shares no more than one chlorine atom. Tornesit is used mainly in solution as a protective coating.

Chapter Eleven

Properties and Tests of Plastics

Introduction

11-1. Necessity for Testing.—In order that one may select the best plastic material to suit a particular application, it is necessary to be able to compare typical properties of the various materials. For this purpose a number of different kinds of tests have been made on plastics, and the results of these tests are used to indicate the suitability of a material in meeting the specific requirements for a particular use. In many cases, it is necessary to make a special test on a certain material to determine whether or not the material is likely to give satisfactory service. Testing therefore plays an important part in the plastics industry.

To illustrate the significance of the results of tests, it will be assumed that a plastic material with a very high dielectric strength and a fair impact strength is sought. The polystyrenes have the highest dielectric strength, and their impact strength is sufficient for ordinary purposes. As another example, it will be assumed that a molded article is to be used in freezing temperatures. A sample article is made of a material that is expected to be satisfactory, and this sample is subjected to conditions similar to those to be withstood in actual usage, before it is definitely decided to use that material.

Tests are divided into special tests and common tests. There are no standard procedures for special testing, but the more common properties, such as tensile strength, dielectric strength, and impact strength, are determined by standardized testing methods.

11-2. Characteristic Properties.—Properties of plastic materials are classified as follows: physical, electrical, thermal, chemical, and optical. The physical properties, for example, will tell how the material stands up under impact, pressure, and stretching. The electrical properties serve to give the user of a plastic material information regarding the extent to which the material will resist the passage of an electric current, and therefore enable the user to decide where the material can be used in electrical applications.

Thermal properties are also important values, as the ability of a material to withstand heat is a limiting factor in such applications as motors, stoves, electric irons, and handles for teakettles and coffee makers. Chemical properties take into consideration the effect of various solutions on the stability of plastics. Many plastic materials are undesirable for a certain application because the common solvents, such as alcohol, gasoline, benzine, etc., have a deteriorating effect on them. Optical properties must be considered in applications, such as lenses and safety glass, where the transmission of light is all-important.

Physical Properties

11-3. Specific Gravity.—An overcoat button made of wood weighs less than an iron button of the same size. The significance of this statement is that the value of the specific gravity for wood is lower than the value for iron. Wood (oak) has a specific gravity of .86, and iron has a specific gravity of 7.8. These values are conveniently found in tables of specific gravities prepared for reference. The specific-gravity value is a relative number, since specific gravity is defined as the weight of a given volume of a substance compared with the weight of the same volume of water at a specified temperature. Comparatively speaking, everyone knows that wood is lighter than iron; but, to find out how much lighter wood.is than iron, it is necessary to compare their specific gravities. If the spaces occupied by a pound of wood and a pound of iron are compared, it will be found that the volume of wood is roughly nine times that of iron.

The molder pays particular attention to the specific gravities of plastic materials, in order that he may evaluate them correctly. If two plastic materials are alike in general properties and cost per pound, and a choice of one must be made, the one with the lower specific gravity will be chosen. The material having the lower specific gravity gives a greater monetary return, since more parts can be molded from a pound of it.

11-4. Determination of Specific Gravity.—The specific gravity of a molded part is easily determined by weighing it first in air and then in water. The principle involved is a simple physical law which states that a body submerged in water is buoyed up by a force which is equal to the weight of its volume of water. A beam

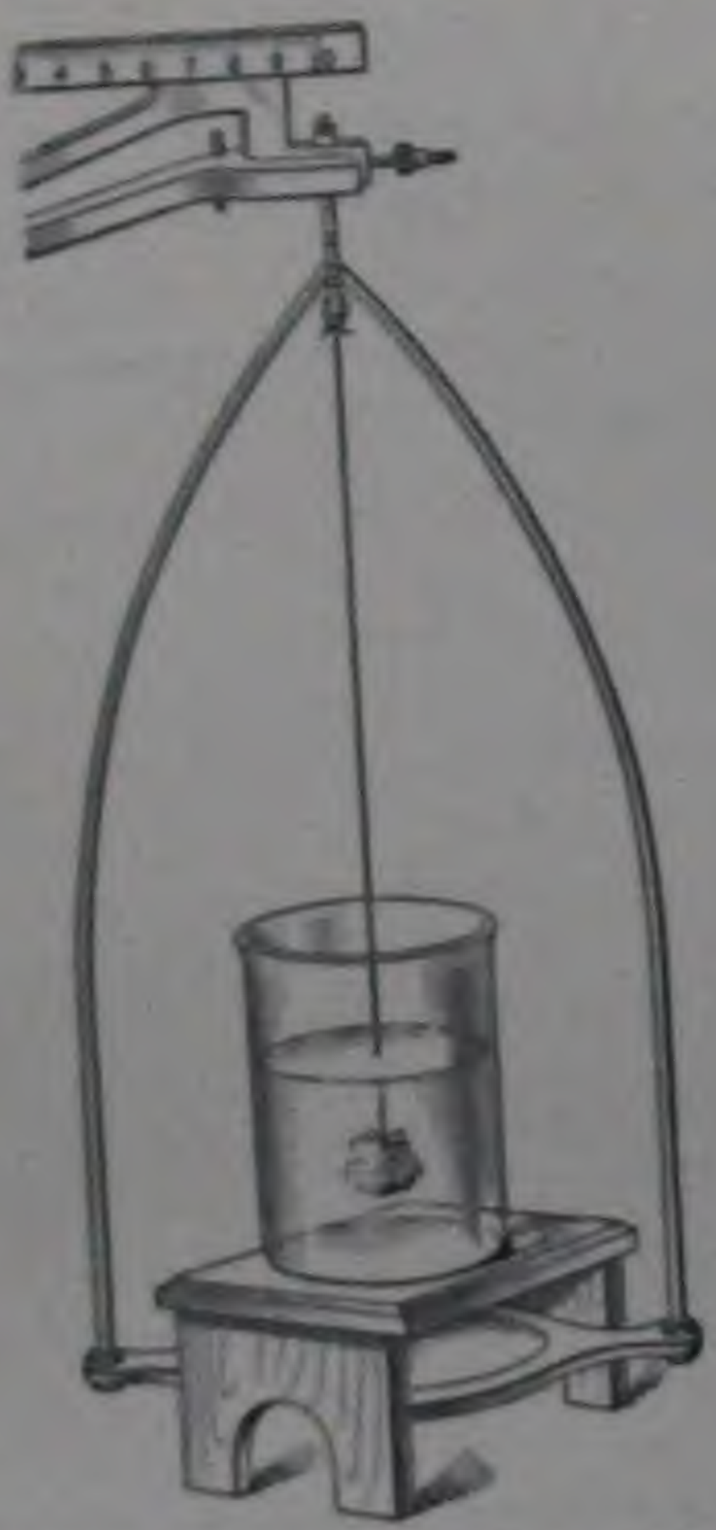


Fig. 11-1. Sectional View of Analytical Balance Equipped With Pan Straddle for Specific Gravity Determination.

balance is used to determine the weight of the molded part in air. The part is then attached by a wire of non-rusting material or a fine cord of non-absorbent material to one end of the balance and is allowed to become completely immersed in distilled water, as shown in Fig. 11-1. All the air bubbles clinging to the part should be removed before its weight is recorded. A fine wire can be used to dislodge these air bubbles.

The difference between the weight in air and the weight in water is the weight of a volume of water equal to the volume of the molded part. The specific gravity is calculated by substituting the proper values obtained in the following formula:

$$\text{Specific gravity} = \frac{\text{weight in air}}{\text{weight in air} - \text{weight in water}}$$

It is customary to maintain a constant temperature throughout the determination. The water temperature should be checked and adjusted, if it deviates from 77° F.

If the article has been molded properly, the result is a true measure of the specific gravity of the material. If the molding

TABLE 11-1

SPECIFIC GRAVITIES OF VARIOUS PLASTICS

Material	Specific Gravity
Phenol formaldehyde (molded)	
Transparent	1.28
General purpose	1.25–1.52
Heat resistant	1.59–2.09
Impact	1.37–1.40
Phenol formaldehyde (laminated)	
Paper base	1.30–1.36
Cotton base	1.30–1.36
Asbestos base	1.55–1.80
Phenol formaldehyde (cast)	
No filler	1.30–1.32
Urea formaldehyde	1.45–1.50
Melamine formaldehyde	
Cotton filled	1.49
Asbestos filled	1.70–1.86
Cold molded	
Non-refractory	1.80–2.20
Refractory	1.80–1.90
Casein formaldehyde	1.35
Shellac	1.10–2.70
Vinyl chloracetate	1.30–1.40
Vinylidene chloride	1.70–1.80
Methyl methacrylate	1.10–1.20
Polystyrene	1.00–1.08
Ethyl cellulose	1.10–1.20
Cellulose acetate	1.30–1.40
Cellulose acetobutyrate	1.14–1.22
Cellulose nitrate	1.35–1.40
High acetyl cellulose acetate	1.27

contains air pockets or internal voids that cannot be removed, a false value will be obtained for the specific gravity.

11-5. Specific Gravities of Plastic Materials.—The specific gravity of a plastic material is, in most cases, dependent on the filler in the compound. Since pine-wood flour, for example, has a specific gravity of something less than 1 and mica has a specific gravity of 2.8, it follows that two compounds having the same basic formula but different fillers will have different specific gravities. The amount of filler is also very important. The greater the per cent of high-specific-gravity ingredient, the higher the specific gravity of the final compound; conversely, the lower the amount of high-

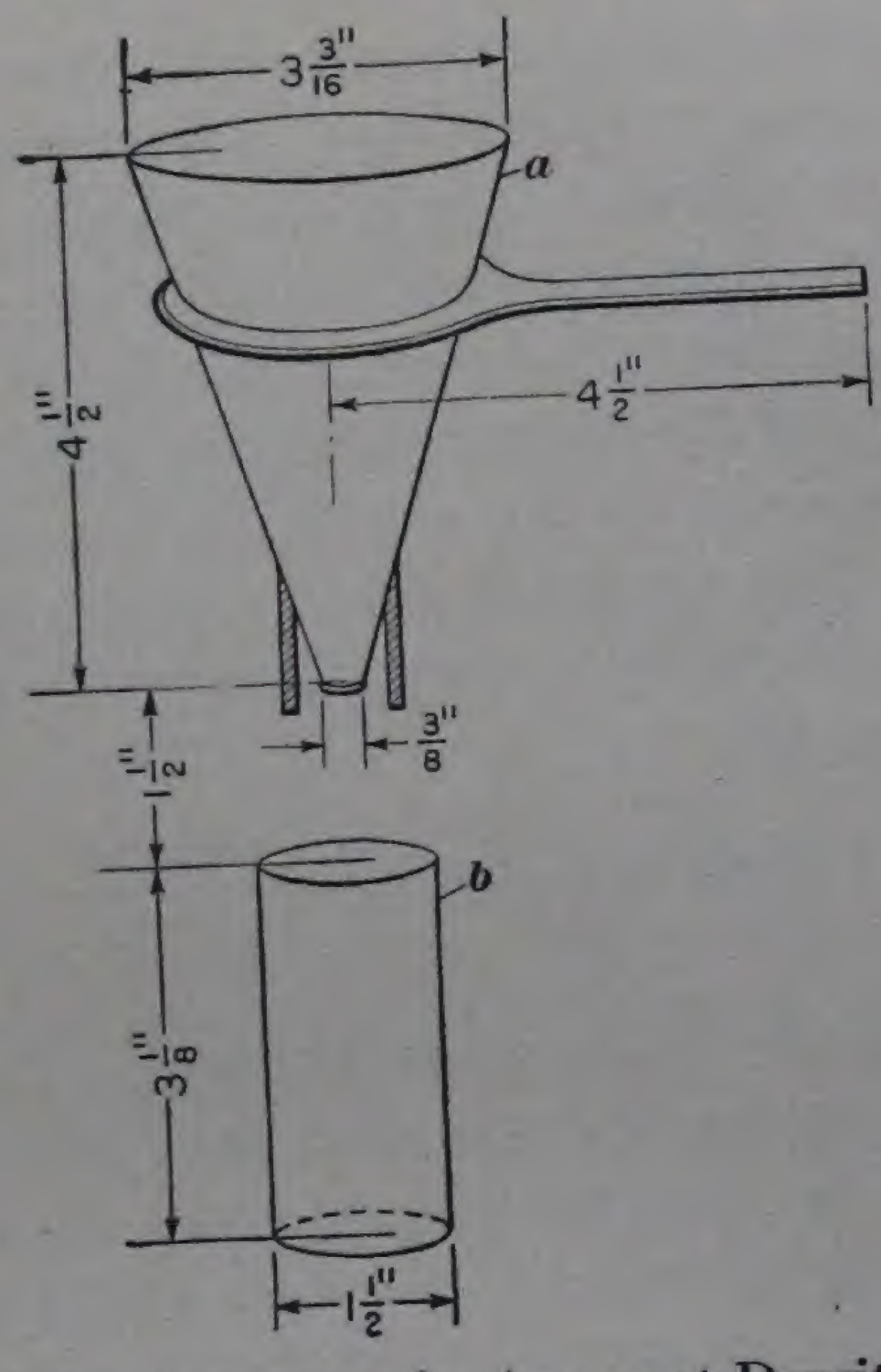


Fig. 11-2. Apparatus for Apparent-Density Test.

specific-gravity ingredient, the lower the specific gravity. Table 11-1 lists the average specific gravities of various plastic materials.

11-6. Apparent Density of Molding Powder.—Specific-gravity tests of the type described in Art. 11-4 are performed only on solid articles. It is difficult to test molding powders because the granules contain entrapped air and gas. For powders and granules an apparent-density test is usually performed. The apparatus required to determine the apparent density of molding powder is shown in Fig. 11-2. The funnel *a* is $4\frac{1}{2}$ inches high. Its larger diameter is $3\frac{3}{16}$ inches and its smaller, or pour-out, diameter is $\frac{3}{8}$ inch. The container *b*, in which the powder is measured, is $3\frac{1}{8}$ inches high and $1\frac{1}{2}$ inches in diameter. Its capacity is 100 milliliters and it is graduated to read with a degree of accuracy within $\frac{1}{2}$ milliliter. The funnel is placed above the container so that the distance from the pour-out to the rim of the container is $1\frac{1}{2}$ inches.

Before proceeding with the test, the empty container must be weighed, and a sample of molding material that is a true representation of the batch must be obtained. To obtain a representative sample, several samples from different parts of the batch are heaped in a pile, which is then divided into quarters. Two quarters

are retained and remixed, and the process is repeated. This method of sampling is known as quartering. The sample obtained in this way, which should be about 50 milliliters, is poured into the funnel and caught in the container beneath it. The mark to which the powder fills the container is recorded, and the container with its contents is weighed. The weight of the powder alone is found by subtracting the weight of the empty container from its weight with the powder. The apparent density, which is the ratio of the weight of the powder to the volume of the powder, is obtained from the following equation:

$$\text{Apparent density} = \frac{\text{weight}}{\text{volume}}$$

11-7. Importance of Apparent Density.—The apparent densities of molding powders serve the molder in more ways than one. In general, it can be said that low apparent densities mean bulky materials. Bulky materials are of much concern to the molder, since they affect the construction and design of molds. Treatments given to materials that are bulky must be entirely different from those given to normal materials. The apparent density of a molding compound gives an insight into the specific gravity of a molded piece. To illustrate, a custom molder had been using 400 grams of a certain molding compound to manufacture a radio cabinet. Upon the acceptance of new molding powders from a materials manufacturer, the molder could not satisfactorily mold the radio cabinet with 400 grams of the new material, but needed 420 grams. The variance in the required amount of molding compound meant that the apparent density of the new material was higher, and the molded material in a radio cabinet had a higher specific gravity. Instead of making specific-gravity tests on radio cabinets, the molder is conveniently forewarned of changes in specific gravity by apparent-density tests on the molding compound.

11-8. Plasticity, or Flow.—The movement of plastic material under heat and pressure is of fundamental importance to a molder, particularly when thermosetting compounds are involved. Of the great variety of articles being molded from thermosetting materials, some are small and thin, others are large and bulky, and still others contain intricate inserts. All of these shapes can be made from one basic plastic material, but the material must vary in

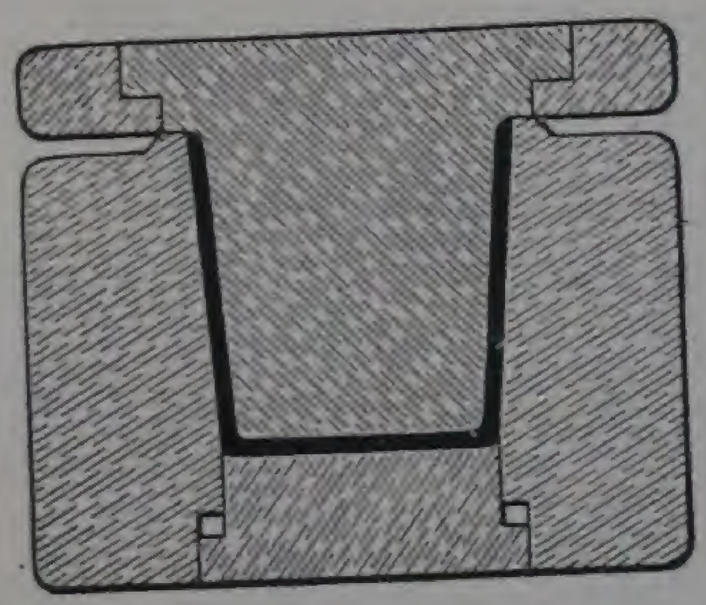


Fig. 11-3. Cup Mold for Determining Plasticity of Material.

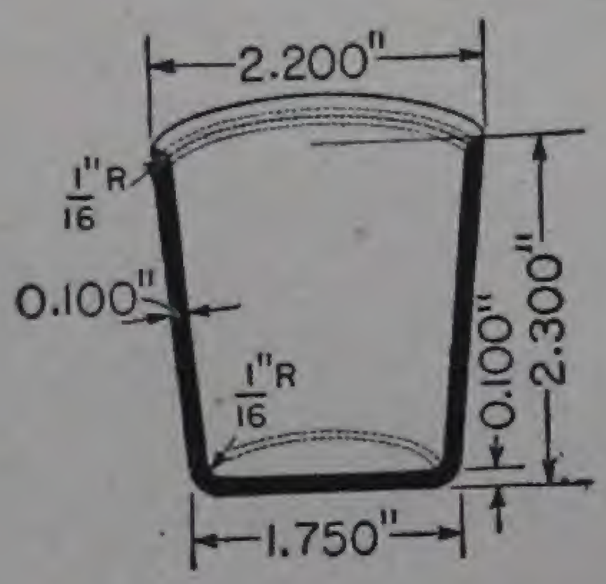


Fig. 11-4. Sectional View of Molded Plastic Cup.

degree of plasticity, or flow. There are several standard methods for determining the rapidity with which a material will take the shape of a mold and the comparative flows of different materials.

11-9. Cup-Mold Test.—One of the methods by which plasticity is determined uses a cup mold such as the one shown in Fig. 11-3. A stop watch to measure short intervals of time and a molding press that is hand-operated or automatic are also necessary in performing the test. Standard conditions of temperature and pressure must be established for the mold before molding data are collected, the usual temperature being 310° F and the pressure 500 pounds per square inch. The temperature and pressure will vary with the type of material. If standard conditions are not established for the mold, test results would have no uniformity; and their validity, especially when later experiments are performed with the same or a different material, would be uncertain. A plastic cup, having the contours and the dimensions shown in Fig. 11-4, is molded between two solid pieces of metal. The upper half of a mold is known as the top force, or plunger, and the bottom half is called the bottom force, or cavity.

When the mold is at the desired temperature, a representative sample of molding powder, which is exactly 15 per cent heavier than the net weight of the cup to be molded, is placed in the cavity. Pressure is then applied, and the stop watch is started at the instant at which the force plug presses against the molding powder. The material resists the closing of the mold until the heat and pressure soften the material, in which condition it flows to every part of the mold. At the instant at which the mold halves come in contact with each other, the watch is stopped; and the elapsed time is recorded. This time represents the flow, or plasticity, of the

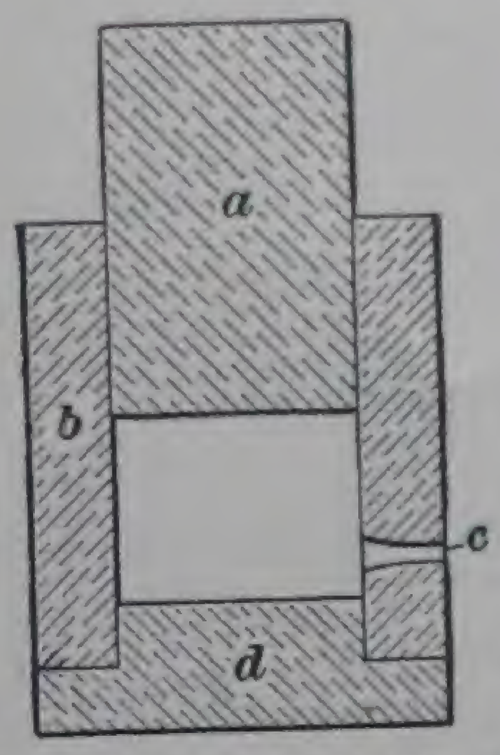


Fig. 11-5. Extrusion Mold for Determining Flow of Material.

material. In general, it can be said that the harder the material, the longer it will take the mold to close.

11-10. Extrusion-Mold Test.—A second method for determining flow employs an extrusion mold similar to the one shown in Fig. 11-5. The plunger *a* transmits pressure to the material contained within the walls *b* of the mold. The orifice *c* is the only outlet for the material, once it has begun to flow. The entire mold is mounted on a mold base *d*. The extrusion test is based on the principle that a certain amount of material, when forced through a small opening, or orifice, under set conditions of temperature and pressure, takes a certain length of time to pass through the orifice. Besides the mold, a stop watch, a steel rule, and a means of supplying constant pressure are necessary. Before the test is begun, the molding powder is compressed into a compact circular disk, or preform, which has a diameter slightly less than that of the mold.

Preforming is a general practice in a molding plant to facilitate the handling of molding powders. The preform is placed in the mold, which has been heated to the proper temperature, and a constant pressure is applied immediately for a definite period of time. The material, which is under heat and pressure, flows out of the orifice of the mold. At various intervals of time the length of the extrusion is measured. The relationship of time to length may be conveniently represented graphically, as shown in Fig. 11-6. By a study of the curved lines of the graph for various materials, the nature of the plasticity, or flow, of each material can be analyzed. For example, if a material flows a distance of 3 inches in 2 minutes, it is softer than a material that flows 3 inches in 3 minutes. Plots, or graphs, of this kind are helpful in comparing

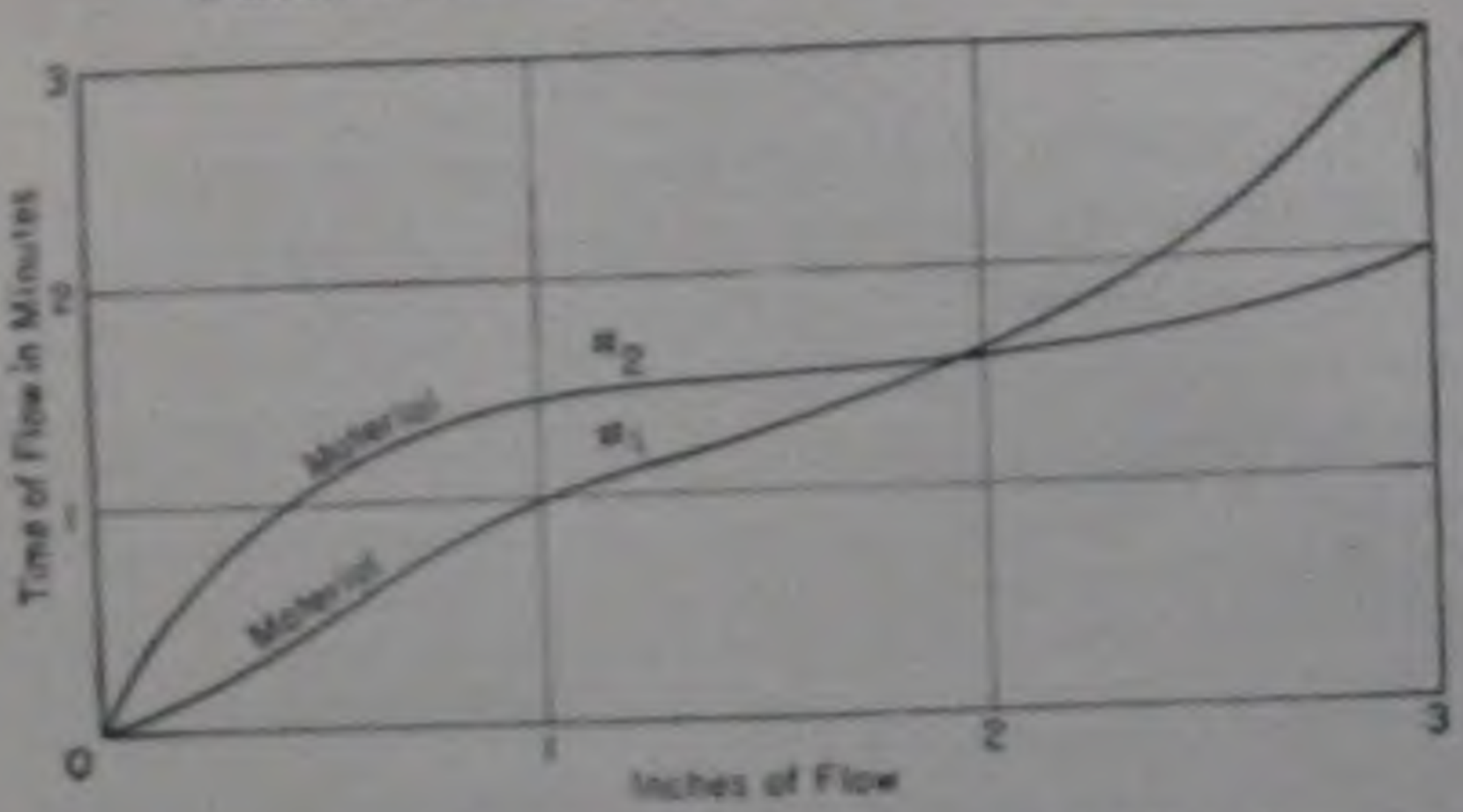


Fig. 11-6. Flow-Time Curves for Different Molding Powders.

various types of molding powders with respect to their time of fluxing, their rate of flow, and their over-all time for flow to cease. In some cases, the amount of material extruded is weighed. The In other words, the comparison is based on weight rather than on distance. There are several standard types of equipment for this test, the most common being the Tinius Olsen tester, which graphically records the flow of material from start to finish.

11-11. Molding Pressures.—The values given in Table 11-2 for molding pressure are for general and ordinary cases. These values cover a wide range of flows and formulas of the same plastic material, and are dependent on correct mold design and molding conditions. Different methods of molding require different pressures. The method of molding for each material is shown, and the corresponding pressure is expressed in pounds per square inch.

11-12. Molding Temperature.—All plastic materials require heat and pressure to make them flow to produce a molded article. The temperature and the pressure are inversely related; in other words, if the pressure is increased, the temperature must be decreased. A plastic article may be produced by using a temperature of 300° F and a pressure of 3,000 pounds per square inch. The same article may be produced from the same material at a temperature of 270° F, but the pressure must be increased to about 3,500 pounds per square inch. The hardness or softness of the material plays an important part in the temperature-to-pressure ratio. The values listed in Table 11-3 represent the best practical

TABLE 11-2

MOLDING PRESSURES FOR VARIOUS PLASTICS

Material	Method of Molding	Pressure Pounds per Square Inch
Phenol formaldehyde (molded)		
Transparent	Compression	2,000–5,000
General purpose	Compression	2,000–4,500
Heat resistant	Compression	2,000–6,000
Impact	Compression	2,000–8,000
Phenol formaldehyde (laminated)		
Paper base	Compression	1,000–3,000
Cotton base	Compression	1,000–3,000
Asbestos base	Compression	1,000–3,000
Phenol formaldehyde (cast)		
No filler	Cast	
Urea formaldehyde	Compression	1,500–6,000
Melamine formaldehyde		
Cotton filled	Compression	1,500–6,000
Asbestos	Compression	1,000–4,000
Cold molded		
Non-refractory	Compression	2,000–4,000
Refractory	Compression	1,000–2,000
Casein formaldehyde	Compression	2,000–2,500
Shellac	Compression	1,000–1,200
	Injection	1,000–2,500
Vinyl chloracetate	Compression	1,500–2,000
	Injection	18,000–30,000
Vinylidene chloride	Compression	500–5,000
	Injection	10,000–30,000
Methyl methacrylate	Compression	1,000–3,000
	Injection	10,000–30,000
Polystyrene	Injection	10,000–30,000
Ethyl cellulose	Compression	1,500–5,000
	Injection	3,000–30,000
Cellulose acetate	Compression	500–5,000
	Injection	8,000–30,000
Cellulose acetobutyrate	Compression	500–5,000
	Injection	8,000–30,000
Cellulose nitrate	Extrusion	2,000–4,500
High acetyl cellulose acetate	Compression	2,500–5,000
	Injection	3,000–30,000

range for each given plastic material. The method of molding for each material is also listed, for conditions differ with the method of molding.

11-13. Cure by Boiling-Water Immersion Method.—The test for cure applies to thermosetting materials alone, since only they

TABLE 11-3

MOLDING TEMPERATURES FOR VARIOUS PLASTICS

Material	Method of Molding	Temperature Degrees F
Phenol formaldehyde (molded)		
Transparent	Compression	300–340
General purpose	Compression	280–360
Heat resistant	Compression	270–350
Impact	Compression	270–350
Phenol formaldehyde (laminated)		
Paper base	Compression	270–350
Cotton base	Compression	270–350
Asbestos base	Compression	300–350
Phenol formaldehyde (cast)		
No filler	Cast	Kettle temp.*
Urea formaldehyde	Compression	270–310
Melamine formaldehyde		
Cotton filled	Compression	280–340
Asbestos filled	Compression	280–330
Casein formaldehyde	Compression	200–225
Shellac	Compression	220–240
	Injection	180–260
Vinyl chloracetate	Compression	280–325
	Injection	280–300
Vinylidene chloride	Compression	220–350
	Injection	250–340
Methyl methacrylate	Compression	280–370
	Injection	325–500
Polystyrene	Injection	375–500
Ethyl cellulose	Compression	300–360
	Injection	350–425
Cellulose acetate	Compression	260–390
	Injection	340–450
Cellulose acetobutyrate	Compression	260–370
	Injection	340–420
Cellulose nitrate	Extrusion	180–250
High acetyl cellulose acetate	Compression	340–370
	Injection	370–440

* Kettle temperature is the temperature of the kettle at the time of the reaction.

have a known cure. There are two kinds of tests for cure: a boiling-water immersion method for urea plastics and an acetone-extraction method for phenolics. Cure is defined as the length of time necessary to allow the binder to become entirely insoluble and infusible. In some cases, the time allowed by a molder to accomplish cure is insufficient. The tests for cure primarily concern them-

selves with the degree of cure; that is, with whether or not the uncured portion of the binder will be harmful in the finished article.

An undercured urea product will undergo hydrolysis and break down in boiling water. To perform the test, the part to be tested is placed in boiling water for 15 minutes. At the end of the boiling period, the article is removed and set out to dry. If the cure is incomplete, a chalking, or whitening effect, on the surface will be observed as drying progresses. The degree of undercure can be estimated by the amount of chalking.

There is, on the other hand, such a condition as overcure, although no test is needed to determine it. Overcure reveals itself as bad discoloration or blisters in the molded article. In the molding of urea articles, thick sections show a tendency to undercure at the center of the section and to overcure at the surface.

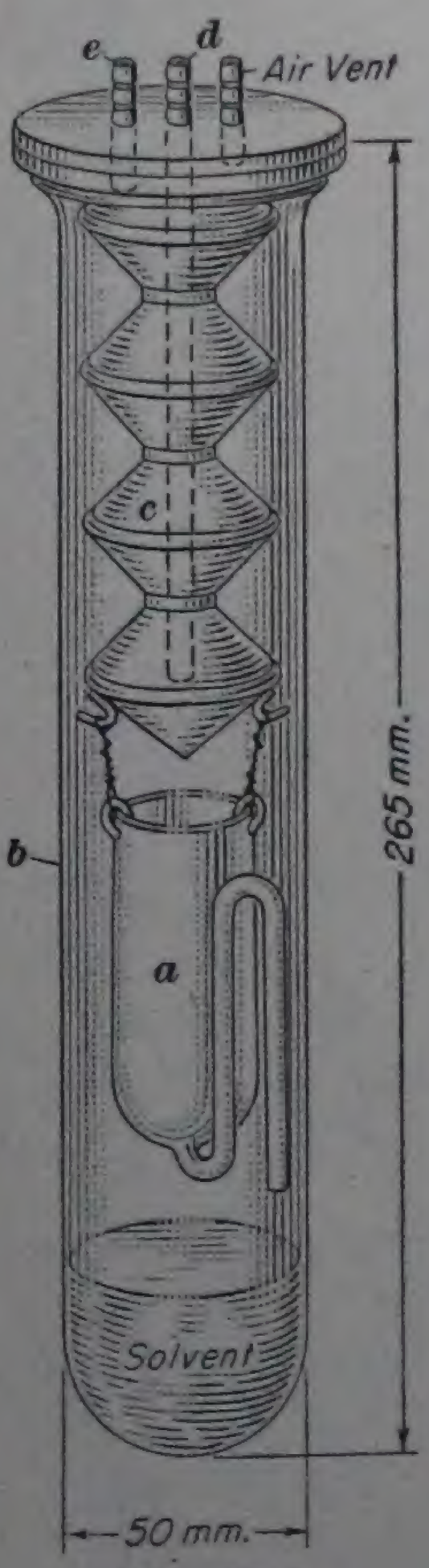


Fig. 11-7. Wiley-Richardson Type of Extraction Apparatus.

11-14. Acetone-Extraction Test.—The acetone-extraction test is used for determining undercure in phenolic plastic parts. A molded part, taken as a sample, is crushed to fine particles that are able to pass a 40-mesh wire screen, which is a standard screen having 40 openings per linear inch. In preparing the sample, care must be taken that no heat is introduced, because heat has a curing effect on phenolic resins that would interfere with the test result. A definite amount of sample is weighed by use of an analytical (or other sensitive) balance and is placed in the vessel *a* of the Wiley-Richardson extraction apparatus shown in Fig. 11-7. This vessel is suspended in a hard-glass tube *b*, which is 50 millimeters in diameter and 265 millimeters in length. A surface condenser *c*, which is attached to the tube cover, receives water at the inlet *d* and discharges it at the outlet *e*. The vessel *a* is so arranged below the condenser that it catches fluid vapors which liquefy on the surface of the condenser. Thus, the fluid drips slowly on the material in the vessel.

The principle of the test is based on the solubility of uncured resin in acetone; therefore, a measured amount of acetone, 50 milliliters, is placed in the tube *b* of the extraction apparatus. The condenser water is then turned on, and heat is applied to the acetone. An oil or a water bath is generally recommended for heating the extractor contents. As the vapors of acetone rise, they are condensed to a liquid on the surface of the condenser, and the liquid drops into the vessel *a*. The acetone dissolves any uncured resin with which it comes in contact, and the solution is discharged, or dumped, from the vessel through the siphon outlet when it reaches a certain level.

The heat should be regulated so that the acetone is dumped at intervals of about 4 minutes. After the extraction has been continued for a period of 4 hours, the sample is removed from the apparatus and carefully dried. The dried sample is weighed, and the dissolved amount, in per cent, is calculated by means of the following formula:

$$\text{Per cent of acetone-extractable matter} = \frac{\text{weight of (vessel + extract)} - \text{weight of vessel}}{\text{weight of sample}} \times 100$$

Some analysts prefer to evaporate the solvent after the extraction has been made and then to weigh the residue.

There is no set standard for the amount of soluble matter that may be present. According to one set of specifications of the United States Bureau of Ships, 5 per cent of soluble matter is allowed in a general-purpose material, 8 per cent in a high-impact colored material, and 6 per cent in a high-impact black material.

11-15. Significance of Cure Test.—It is important for the molder to know that the articles he produces will satisfactorily meet the field tests. Highly undercured parts are usually weak in mechanical strength. Cure also has an important effect on the ability of a plastic part to withstand the weather and varying temperatures. The molder usually tests for cure when he sets the cycle of manufacture. The cure time in the press must be long enough to minimize the amount of acetone-soluble matter. Cure tests are sometimes run as spot checks to determine whether the production is up to par.

11-16. Cold Flow.—Some plastics, when compressed or stretched, will not regain their original dimensions on the removal of the deforming force. The distortion produced is known as cold flow. This characteristic should not be confused with the deformations produced by loads that exceed the elastic limit of the material. Cold flow is the tendency to distort under loads that are lower than the elastic limit. This property is important, especially where metals and plastics are to be used in the same application, for the following reason. For example, let it be assumed that a metal name plate is riveted onto a plastic part. When the rivet is forced into the plastic material, it actually compresses part of the material. No two materials can occupy the same place at the same time and, since the over-all dimensions of the plastic part remain the same, the material must be compressed. If the material tends to undergo cold flow, the distortion will become permanent and the rivet will become loose. If the material has a good resistance toward cold flow, it will resist the applied compression, and hence will hold the rivet tight.

There is no standard test for cold flow. Of the variety of tests in use, the one generally accepted is to load a sample in the form of a $\frac{1}{2}$-inch cube with 1,000 pounds for a period of 24 hours. All plastic materials have compressive strengths that greatly exceed 4,000 pounds per square inch; so the load factor and the compressive-strength factor do not enter into the values for the test. The difference between the heights of the sample before and after the load is applied is a measure of the tendency of the material toward cold flow. The value is expressed in per cent, the calculation being made by using the following formula:

$$\text{Per cent of cold flow} = \frac{H_b - H_a}{H_b} \times 100$$

in which H_b = height of sample before load is applied;
H_a = height of sample after load has been applied.

If the material has no cold flow, H_b and H_a will be the same.

11-17. Tensile Strength.—Tensile strength is one of the important physical properties of a material. Industry interprets it to mean the ability of a part to withstand certain loading conditions. For example, the material used in building a bridge must be strong enough to carry the load that the bridge must withstand.

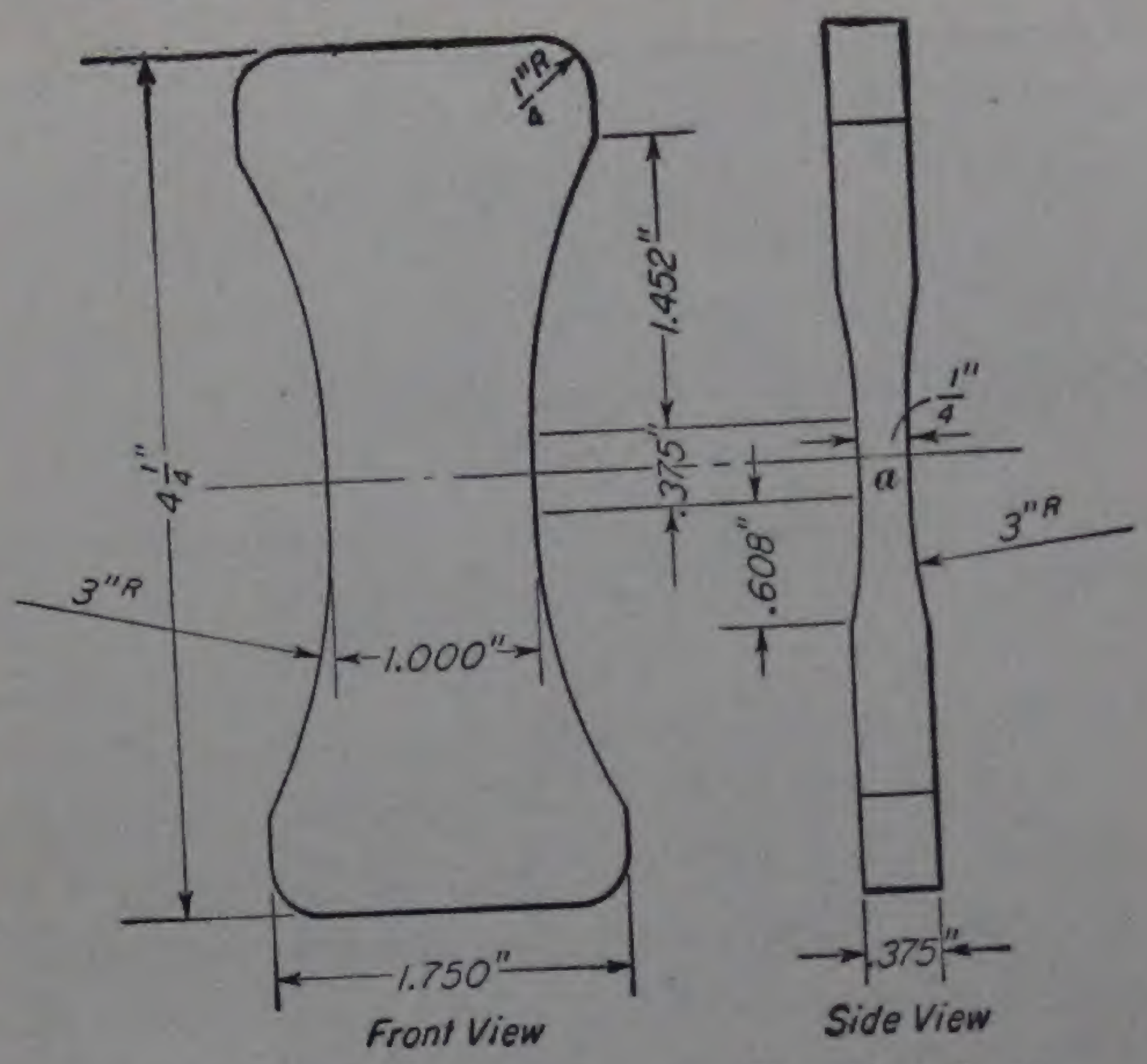
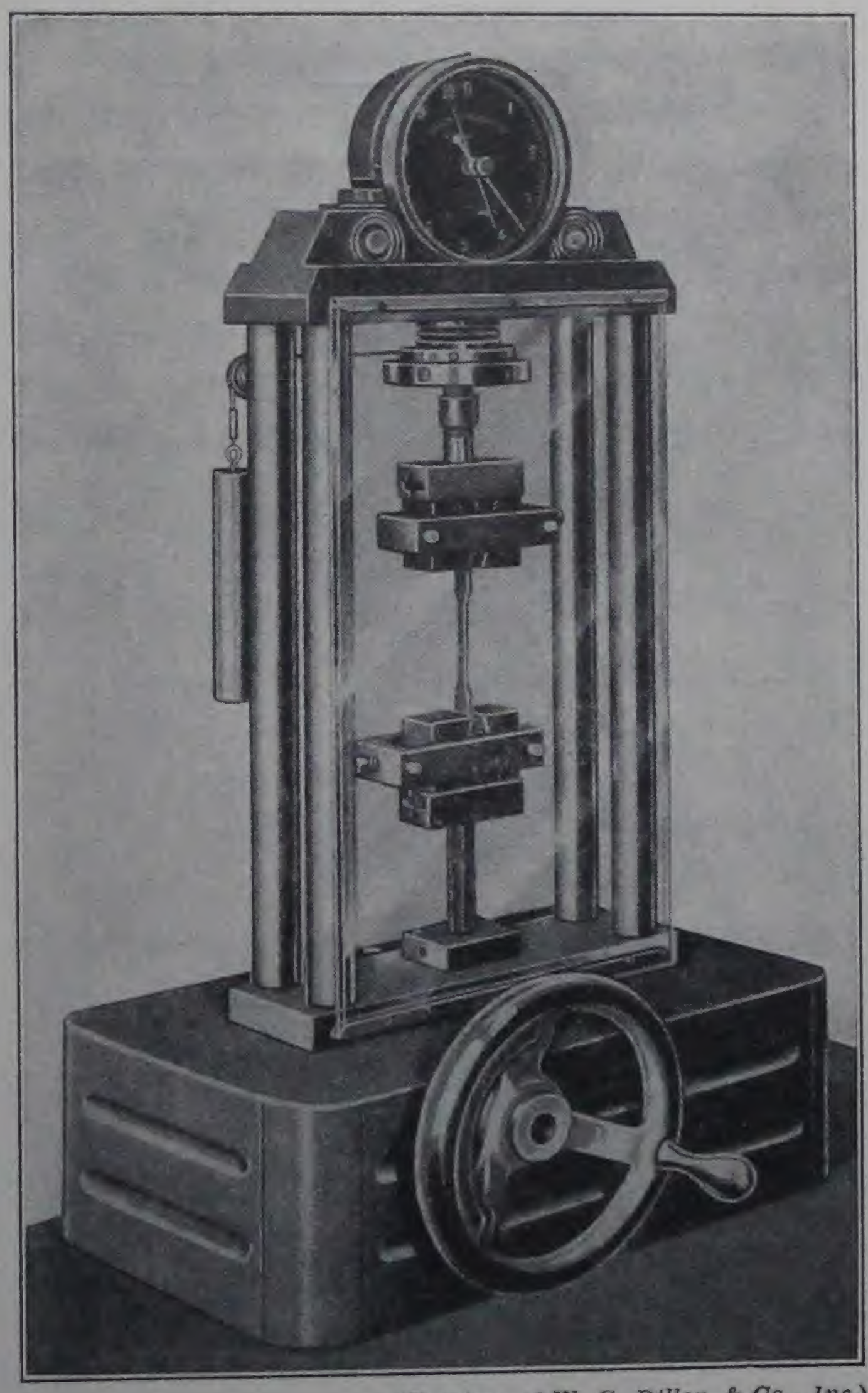


Fig. 11-8. Standard Tension-Test Specimen.

In the field of plastics, a material must be strong enough to fulfil the mechanical requirements of its application.

Tensile strength is defined as the resistance which a material offers to being pulled apart. If a bar of molasses candy, for example, were firmly grasped in two hands, the force required to pull the bar apart would represent the tensile strength of the bar. All plastic materials undergo a standard test for determining their tensile strengths. There are, however, many factors that influence the tensile strength of a material, and these are reflected in the actual test. Theoretically, phenolic molding powder possesses tensile strength, but that strength can be measured only if the material is converted into a test sample by molding. During this conversion the factors influencing tensile strength come into play. If the material is undercured, the strength will be low. An insufficient molding pressure produces the same effect as does a low molding temperature.

The actual test for tensile strength may be conducted under different conditions. The conditions of the test are governed by the requirements of the application. If a molded part must have a tensile strength of 6,000 pounds per square inch at a temperature of $-20°$ F, the tests must be run on samples that have been subjected to that temperature. No matter what the conditions of the test may be, the test itself is always the same. Before testing,



(*Courtesy of W. C. Dillon & Co., Inc.*)

Fig. 11-9. Dillon Tensile-Testing Machine.

samples may be permitted to age at room temperature for several days, or they may be kept under a certain humidity for a specified period of time.

For most plastic materials, the test specimen is a long bar of rectangular cross-section with enlarged ends. A specimen having the form illustrated in Fig. 11-8, which is usually referred to as a figure-eight or a dog biscuit, is required for the tensile-strength test on some materials. The specimen illustrated has a cross-sectional area of $\frac{1}{4}$ square inch at the middle, but the area may be as large as 1 square inch or as small as $\frac{1}{20}$ square inch under certain conditions.

11-18. Dillon Tensile Tester.—In making a tensile test, the ends of the specimen are placed in the holding jaws of a testing machine, such as the Dillon tensile tester shown in Fig. 11-9. The upper jaw is attached to a rod that is connected to the mechanism of the gage at the top of the machine. The lower jaw is fastened to a screw that extends down into the base of the tester. On the lower end of the screw is a nut that can be rotated by turning the counterbalanced hand wheel. When the wheel is turned, the rotation of the nut causes a downward movement of the screw, and thus a pull is exerted on the test specimen. The amount of this pull is registered on the gage at the top, and the hand wheel is turned until the pull is great enough to break the test piece. There are two pointers on the gage, known as a live pointer and a dead pointer. As the pull increases, the live pointer swings around clockwise, carrying the dead pointer with it. When the test specimen breaks, the pull on the upper jaw is released, and the live pointer returns to zero; but the dead pointer remains where it was, and the figure to which it points is then the maximum pull, in pounds, exerted on the test specimen. This pull, divided by the cross-sectional area of the specimen, in square inches, at the point where it breaks is the tensile strength of the material, in pounds per square inch.

The testing machine illustrated can record a maximum pull of 10,000 pounds. If, therefore, material having a tensile strength greater than 10,000 pounds per square inch is to be tested, the specimen used must have a cross-section of less than 1 square inch at its smallest part; otherwise, sufficient pull to break it cannot be exerted. By reducing the cross-section of the specimen sufficiently, materials having tensile strengths as great as 200,000 pounds per square inch can be tested.

The gear ratio between the hand wheel and the rotating nut on the screw is 40 to 1. One turn of the nut pulls the screw down $\frac{1}{8}$ inch. Thus, 40 turns of the hand wheel are needed to move the screw $\frac{1}{8}$ inch.

11-19. Specifications for Tensile Strength.—Practically any standard testing machine may be used in the tensile-strength test. The Bureau of Ships of the United States Navy Department, in its Specification 17P4(INT), suggests the following conditions under which samples should be tested:

Condition 1—Specimen tested as received.
Condition 2—Specimen conditioned for no less than 96 hours at a temperature of 77° F and a relative humidity of 70 per cent.
Condition 3—Specimen submerged in water at 77° F for 24 hours, then submerged for 48 hours at 122° F. Specimen is dried and tested.
Condition 4—Specimen submerged in 77° F water for 24 hours, 122° F water for 48 hours, 212° F water for 6 hours. Specimen is dried and tested.

The specification requires the following tensile strengths for these conditions:

Condition 1—6,200 pounds per square inch.
Condition 2—6,000 pounds per square inch.
Condition 3—6,000 pounds per square inch.
Condition 4—5,800 pounds per square inch.

11-20. Tensile Strengths of Plastic Materials.—The tensile strength of a plastic material depends primarily on the formulation. The material cannot have a tensile strength greater than that of the strongest of the constituents. To achieve the maximum strength of the material, the molding conditions must be practically perfect. A temperature that is too high may cause the material to burn, and a temperature that is too low may cause incomplete fusion; either condition results in low tensile strength. Similarly, a pressure that is too high or too low causes tearing of the fiber or incomplete binding, either one causing a loss of tensile strength. The values given in Table 11-4 represent the ranges of tensile strengths for various plastic materials.

11-21. Compressive Strength.—In contrast to tensile strength, which manifests itself as a resistance to being pulled apart, compressive strength is the resistance of a material to being crushed under an applied load. Compressive strength is not so important a property as tensile strength and shearing strength; nevertheless, it bears a unique relation to these other mechanical strengths. The compressive strength of a material is determined from a molded sample. The conditions of molding the sample will have a distinct bearing on the values obtained in testing. As a general rule, the samples are molded under conditions of time, temperature, and pressure expected to produce the best qualities of the material. However, in rare cases where compressive strength must meet a specification, the tests are run under the specified conditions. The test specimen is usually a cube with $\frac{1}{2}$-inch sides. The test itself may be run on any standard testing machine which also

TABLE 11-4

TENSILE STRENGTHS OF VARIOUS PLASTICS

Material	Tensile Strength Pounds per Square Inch
Phenol formaldehyde (molded)	7,000–12,000
Transparent	5,000–8,000
General purpose	4,000–8,000
Heat resistant	5,500–8,000
Impact	
Phenol formaldehyde (laminated)	7,000–18,000
Paper base	8,000–12,000
Cotton base	7,000–12,000
Asbestos base	
Phenol formaldehyde (cast)	8,500–10,000
No filler	5,500–7,000
Urea formaldehyde	5,000–7,000
Melamine formaldehyde	5,500–7,000
Cotton filled	
Asbestos filled	
Cold molded	1,000–3,000
Non-refractory	900–1,600
Refractory	7,000–9,000
Casein formaldehyde	900–2,000
Shellac	8,000–10,000
Vinyl chloracetate	4,000–7,000
Vinylidene chloride	4,000–7,000
Methyl methacrylate	5,000–9,000
Polystyrene	2,000–9,000
Ethyl cellulose	2,800–10,000
Cellulose acetate	2,500–7,000
Cellulose acetobutyrate	5,000–12,000
Cellulose nitrate	3,000–8,000
High acetyl cellulose acetate	

tests for tensile strength. The sample is placed on a firm foundation and a crushing load is then applied. The amount of the load is known at all times. At some time during the test, the specimen will show signs of breaking. At the first sign of breakage, the load should be noted. This load represents the compressive strength of the material, which is expressed in pounds per square inch.

A sample can be tested for compressive strength in either of two ways: parallel to the molding pressure, or at right angles to the molding pressure. The direction of the pressure is an important factor that must always be noted on the report of the test. The load should always be applied at a uniform rate, which should be

TABLE 11-5

COMPRESSIVE STRENGTHS OF VARIOUS PLASTICS

Material	Compressive Strength Pounds per Square Inch
Phenol formaldehyde (molded)	
Transparent	10,000–30,000
General purpose	16,000–36,000
Heat resistant	18,000–36,000
Impact	20,000–32,000
Phenol formaldehyde (laminated)	
Paper base	20,000–40,000
Cotton base	30,000–44,000
Asbestos base	18,000–45,000
Phenol formaldehyde (cast)	
No filler	20,000–25,000
Urea formaldehyde	22,000–26 000
Melamine formaldehyde	
Cotton filled	15,000–17,000
Asbestos filled	7,500–11,000
Cold molded	
Non-refractory	6,000–15,000
Refractory	15,000–17,000
Casein formaldehyde	27,000–50,000
Shellac	10,000–17,000
Vinyl chloracetate	10,000–12,000
Vinylidene chloride	7,500–8,500
Methyl methacrylate	10,000–15,000
Polystyrene	11,000–15,000
Ethyl cellulose	10,000–12,000
Cellulose acetate	5,000–27,000
Cellulose acetobutyrate	7,500–22,000
Cellulose nitrate	20,000–30,000
High acetyl cellulose acetate	5,000–20,000

slow enough to permit any disintegration to be noted at the exact load at which it occurs. If a $\frac{1}{2}$-inch cube is used for the test sample, the result must be expressed on the square-inch basis. If a 1-inch cube is used for the test sample, the load itself will represent the compressive strength of the sample. When determining the compressive strength of a plastic material, at least ten samples should be tested. Any exceedingly high or low individual strengths should be discarded and retests should be made until the strengths of at least ten samples are in fair agreement. The average of these acceptable results should be taken as the compressive strength.

The compressive strengths of various plastic materials are given in Table 11-5. The values for a given material are the mini-

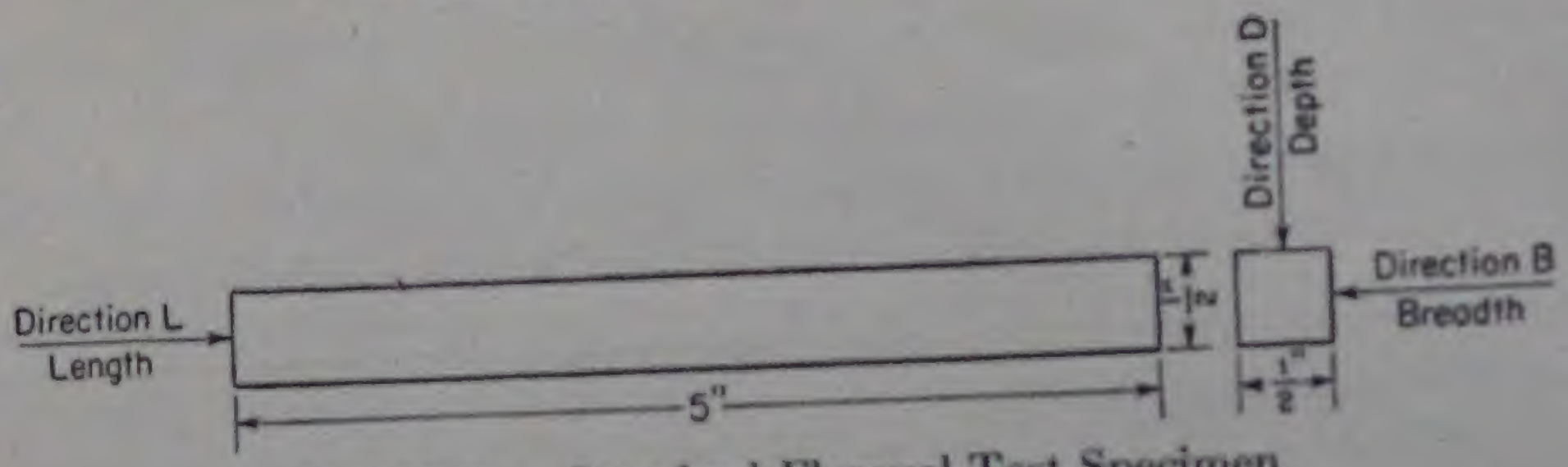


Fig. 11-10. Standard Flexural-Test Specimen.

mum and maximum under various conditions, and represent a variety of flows and formulas of the same plastic material.

11-22. **Flexural Strength.**—Flexural strength represents the bending, or flexing, strength of a material. It is really a combination of tensile and compressive strength. When any sample is being tested for flexural strength, part of it undergoes tensile stress and part undergoes compressive pressure. For example, if an ordinary lead pencil is broken by holding it in both hands and exerting pressure with the thumbs, the part of the pencil next to the thumbs is being compressed, while that part on the side of the pencil away from the thumbs is being torn apart by tensile stress. Since many plastic applications require the material to withstand rather high lateral, or side, pressures, flexural strength is an important physical property. In some instances, a device is used in conjunction with a flexural-strength test to determine the deflection the material will withstand before breakage.

Any universal testing machine may be used to perform the flexural-strength test, which is conducted on molded samples. As in other tests, the conditions of molding and the conditioning of the samples have an important bearing on the result of the test. The samples may be tested at right angles or parallel to the molding pressure. All facts concerning the conditions should be recorded in a test report. The most convenient sample is a bar $\frac{1}{2}$ in. $\times \frac{1}{2}$ in. $\times 5$ in., as illustrated in Fig. 11-10. The test sample is placed on two supporting knife edges that are 4 inches apart. A third knife edge is placed on top of the sample midway between the two supports. The load is applied indirectly to the third knife edge. As the load increases, the sample starts to bend slightly. The load is increased at a uniform rate until the sample breaks. The flexural strength is then calculated by means of the formula

$$S = \frac{3FL}{2BD^2}$$

TABLE 11-6

FLEXURAL STRENGTHS OF VARIOUS PLASTICS

Material	Flexural Strength Pounds per Square Inch
Phenol formaldehyde (molded)	
Transparent	12,000–17,000
General purpose	8,000–15,000
Heat resistant	8,000–15,000
Impact	8,000–13,000
Phenol formaldehyde (laminated)	
Paper base	13,000–20,000
Cotton base	13,000–30,000
Asbestos base	10,000–35,000
Phenol formaldehyde (cast)	
No filler	10,000–12,000
Urea formaldehyde	10,000–13,000
Melamine formaldehyde	
Cotton filled	15,000–17,000
Asbestos filled	7,500–11,000
Cold molded	
Non-refractory	4,000–9,500
Refractory	2,000–5,000
Casein formaldehyde	10,000–18,000
Shellac	
Vinyl chloracetate	12,000–14,000
Vinylidene chloride	15,000–17,000
Methyl methacrylate	10,000–15,000
Polystyrene	8,000–19,000
Ethyl cellulose	4,000–12,000
Cellulose acetate	1,500–18,000
Cellulose acetobutyrate	2,000–13,000
Cellulose nitrate	8,000–10,000
High acetyl cellulose acetate	1,500–12,000

in which S = flexural strength, in pounds per square inch;
F = breaking load, in pounds;
L = distance between supports, in inches;
B = breadth of sample, in inches;
D = depth of sample, in inches.

Table 11-6 lists the flexural strengths of the various plastic materials. The values given for each material represent the minimum and maximum values under different conditions for the various flows and formulas of the same plastic.

11-23. Deflection.—The deflection, or actual movement of the center of the sample, can be measured by attaching a horizontal

pointer to the knife edge that applies the force. A movable scale, which is set up directly in back of the pointer, is set at zero before the the test is started. As the sample bends under the influence of the load applied, the pointer will move with the upper knife edge. The scale should be graduated in divisions of $\frac{1}{32}$ inch. The amount of deflection is then recorded from the scale by noting the displacement of the pointer. While the deflection is not important, it does give an indication as to the chemical composition of the material. A synthetic rubber would show a very high deflection, whereas a urea-formaldehyde molding compound would show a low deflection. The actual stretch of a material is determined by an elongation test. The recording of deflection in the flexural-strength test should be done merely as a matter of form.

11-24. Elongation.—Elongation is the amount of stretch a material shows under an applied load. It is always expressed as a per cent. The per cent elongation is calculated by means of the following formula:

$$\text{Per cent elongation} = \frac{\text{final length} - \text{original length}}{\text{original length}} \times 100$$

The test is performed at the same time as that for tensile strength, but a different factor is observed. In the tensile-strength test, the hand wheel keeps the sample under tension all the time. For the elongation test, two pointers are set in the testing machine so that they are nearly opposite the ends of the sample. A fixed linear scale is set in back of the two pointers, and the exact distance between the pointers is noted before the regular tensile-strength test is started. The amount of the stretch during the test can be readily noted by the movement of the pointer that is attached to the lower jaw. At the point of rupture of the specimen under test, the actual distance that the sample has stretched should be recorded. The elongation is calculated by substituting the correct values in the formula given.

For all practical purposes, thermosetting materials have no elongation. All thermoplastics have a definite elongation, the per cent of elongation depending on the formulation of the plastic. The lower the per cent of plasticizer, the harder the material; the harder the material, the lower the per cent of elongation. The values

TABLE 11-7

ELONGATIONS OF VARIOUS PLASTICS

Material	Elongation Per Cent
Vinylidene chloride	10–40
Methyl methacrylate	5–15
Polystyrene	2–5
Ethyl cellulose	10–40
Cellulose acetate	15–80
Cellulose acetobutyrate	40–80
Cellulose nitrate	10–60
High acetyl cellulose acetate	15–60

given in Table 11-7 are for a range of hard-flow and soft-flow materials in a variety of formulas.

11-25. Shrinkage.—All molded plastic materials show a change in dimension while cooling from the mold temperature to room temperature. The actual difference between the length of the molded piece at room temperature and the length of the mold at room temperature, calculated and reported as inch per inch of molded piece, represents the shrinkage of the material. The factor of shrinkage is very important to the tool maker as well as to the molder. One of the advantages of plastic materials is that the shrinkage can be held to a close tolerance in mass production. One of the reasons why this can be done is that, since the shrinkage factor of each material is always known, the shrinkage in the molding operations can be compensated for.

If an article that has an over-all length of 12 inches is to be molded, the mold must be constructed larger than 12 inches, the amount over the 12 inches depending entirely on the shrinkage factor of the material being used. If the material has a shrinkage factor of .007 inch per inch, for instance, the mold maker must figure that the total shrinkage will equal $12 \times .007$, or .084 inch, and accordingly must build the mold that much larger. When the molded part is first removed from the mold, it is .084 inch oversize; but, when it cools to room temperature, it shrinks at the rate of .007 inch per inch. The part at room temperature several hours later will measure 12 inches.

11-26. Importance of Shrinkage Factor.—Many plastic materials contain inserts. The shrinkage factor of the material is important, since allowances must be made for shrinking around the insert. If no allowance is made, the plastic will crack in shrinking around the insert. The difference in the coefficients of expansion of plastics and metals should always be considered when the two are to be used in a single application.

Shrinkage varies directly with the molding conditions. When thermosetting materials are used, the formula is the primary factor in the amount of shrinkage. In actual molding, the temperature, pressure, and degree of cure all have a bearing on the shrinkage. The more undercured the part, the more the distortion. Thermoplastics, however, since they undergo a physical change only, have a fairly uniform shrinkage regardless of molding conditions. Most molded parts are allowed a tolerance on dimensions. This tolerance may vary, but in most cases it is $\pm .005$ inch.

11-27. Shrinkage Test.—The shrinkage test consists of nothing more than the molding of a bar $\frac{1}{2}$ in.$\times\frac{1}{2}$ in.$\times 5$ in. under standard conditions of temperature, pressure, and cure. For thermosetting materials, the conditions are usually 320° F at a pressure of 4,000 pounds per square inch for a period of 6 minutes. The article is measured between 16 and 24 hours after removal from the mold, and the shrinkage is calculated by comparing the dimensions of the molded article with those of the mold itself.

For thermoplastic materials, the procedure is the same except that the mold must be chilled in order to remove the part. The chilling usually requires about 2 minutes. Care must be taken that the mold is up to temperature before another test is started. The average of several tests is taken as the shrinkage of the material.

11-28. Shrinkage Factors for Plastic Materials.—The published values for mold shrinkage are based on the assumptions that materials are handled under ideal conditions, and are thoroughly cured under correct conditions of temperature and pressure. In actual practice, however, this is not the case, as materials are seldom handled under ideal conditions. Mold-shrinkage values, representing the minimum and maximum values for various flows and formulas of the same plastic, are listed in Table 11-8.

11-29. Impact Strength.—Impact, or shock, resistance is another important physical property of any material. The value

TABLE 11-8

MOLD SHRINKAGES OF VARIOUS PLASTICS

Material	Mold Shrinkage Inch per Inch
Phenol formaldehyde (molded)	
Transparent	.009–.011
General purpose	.006–.010
Heat resistant	.002–.006
Impact	.003–.007
Phenol formaldehyde (laminated)	
Paper base	
Cotton base	
Asbestos base	
Phenol formaldehyde (cast)	
No filler	
Urea formaldehyde	.006–.010
Melamine formaldehyde	
Cotton filled	.008–.011
Asbestos filled	.004–.007
Cold molded	
Non-refractory	.010–.017
Refractory	.001–.010
Casein formaldehyde	
Shellac	.002–.004
Vinyl chloracetate	.000–.001
Vinylidene chloride	.004–.012
Methyl methacrylate	.003–.006
Polystyrene	.002–.008
Ethyl cellulose	.001–.007
Cellulose acetate	.002–.004
Cellulose acetobutyrate	.002–.004
Cellulose nitrate	
High acetyl cellulose acetate	.002–.004

of impact strength is usually expressed in terms of foot-pounds per inch of notch. A foot-pound may be defined as the amount of energy generated by a pound mass falling through a distance of 1 foot. The simplest form of impact test is to crash a known weight, falling through a known distance, against the plastic sample. The process is repeated, with the distance increased after each blow, until cracking or breaking occurs. The main disadvantage of such a test is that no calculation is made for the fatigue factor. The sample tends to get tired under repeated blows and may crack before the true impact strength has been reached. The fatigue can be compensated for by using a new sample for each blow, as the impact is increased. The using of a new sample, however, may lead

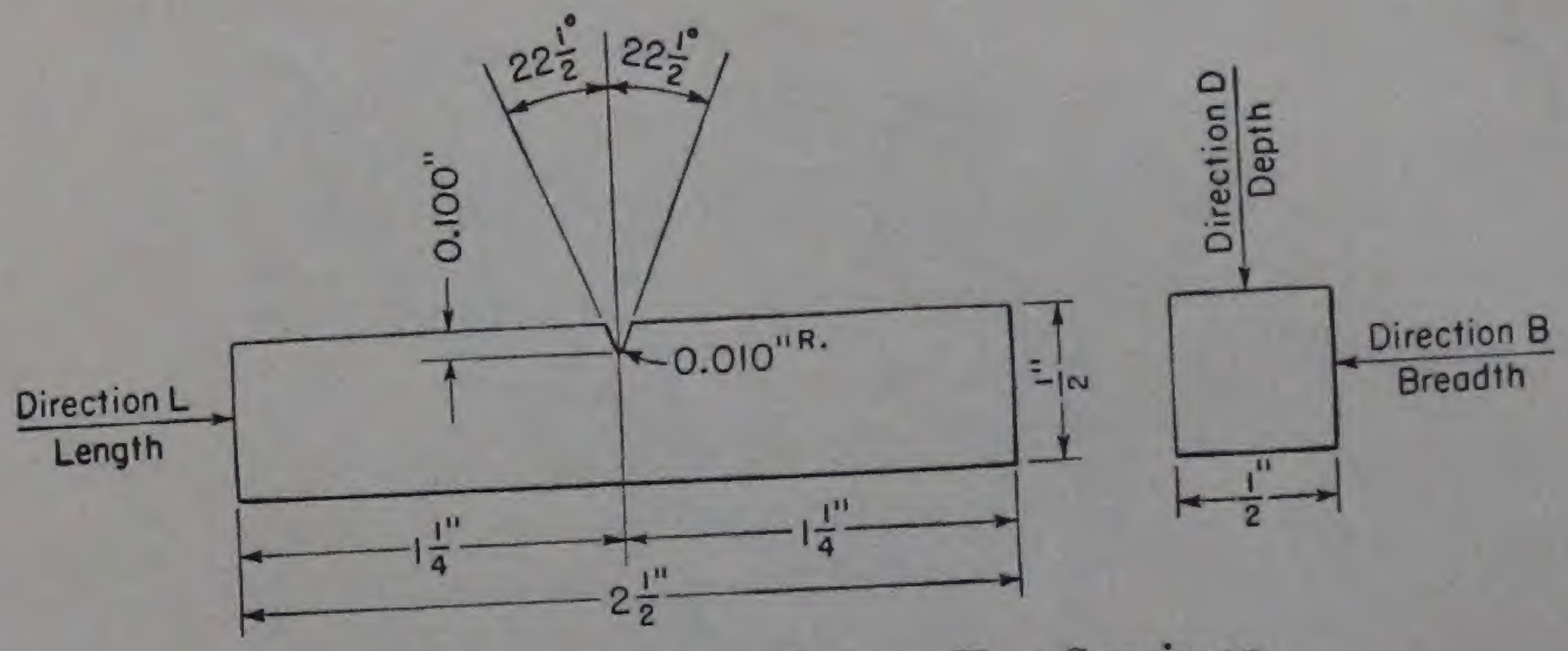


Fig. 11-11. Standard Impact-Test Specimen.

to complications, since it would require absolute uniformity of each sample.

The best method of impact testing has been found to be the pendulum-swing test, in which the sample is placed in such a position that it will be struck squarely by the pendulum at its lowest point of swing. The pendulum swinging through an arc gathers momentum so that, when it strikes an object, it strikes with a definite force. If nothing were in the way of the pendulum, it would swing as high on the back stroke as on the down stroke. Hence, the force may be measured by the distance of the back swing. Two standard machines used for testing impact strength are the Izod machine and the Charpy machine. They are almost identical, the only difference being in the method of placing the test sample in the path of the pendulum.

The standard test sample is illustrated in Fig. 11-11. The samples are usually made by molding a bar $\frac{1}{2}$ in. $\times \frac{1}{2}$ in. $\times 5$ in. and cutting it in half. Each sample is usually notched, that is, it contains a shallow V in the center of one surface. The notch, which may be machined or molded, localizes the break during the test and permits direct and true calculations. Without the notch, the blow might cause breakage at any point in the sample, thereby causing complications in the actual calculation. Since the notch may be made either parallel to the molding pressure or at right angles to the molding pressure, the method of placing the sample is also important, as there is quite a difference in the results between the two placings.

11-30. Impact Test.—In the Izod machine, Fig. 11-12, the sample is gripped vertically in such a way that the notch faces the

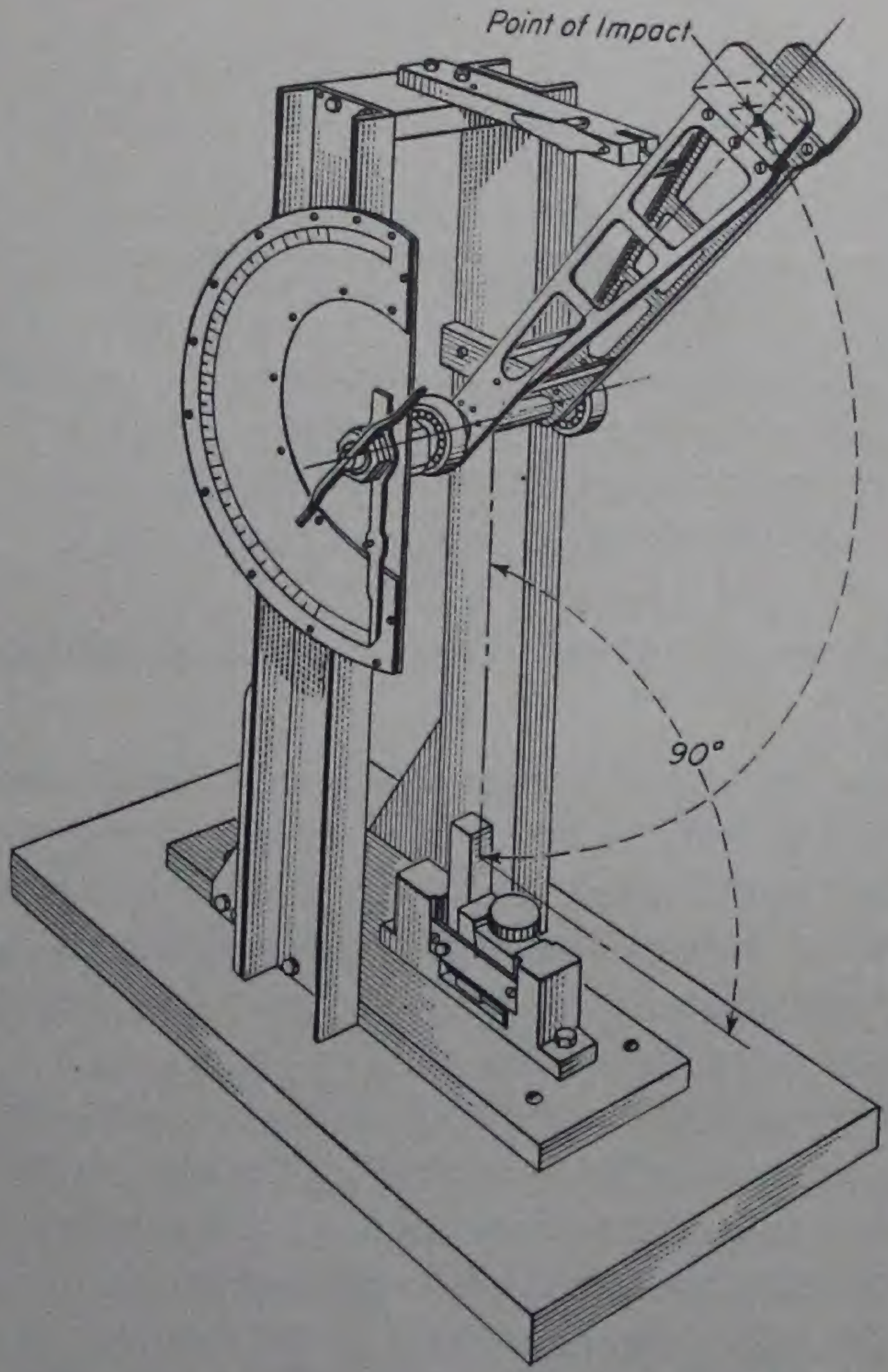


Fig. 11-12. Izod-Type Cantilever-Beam Impact Machine.

blow of the pendulum, which strikes about $\frac{3}{4}$ inch above the gripping point. The notch is set right at the gripping point. The dial of the machine is calibrated so that the impact-strength value is read directly, provided the sample is dimensionally correct. The machine is checked for windage and friction before it is used. The pendulum is placed in the top position and the sample is set correctly in the grips. The hammer is then released, swinging downward in an arc and hitting the sample squarely. Since the sample takes away some of the force of the pendulum, the pendulum does not swing so high on the back stroke. The difference between the height of the down stroke and the height of the back stroke is proportional to the energy lost in breaking the sample and, therefore, it measures the impact strength of the material.

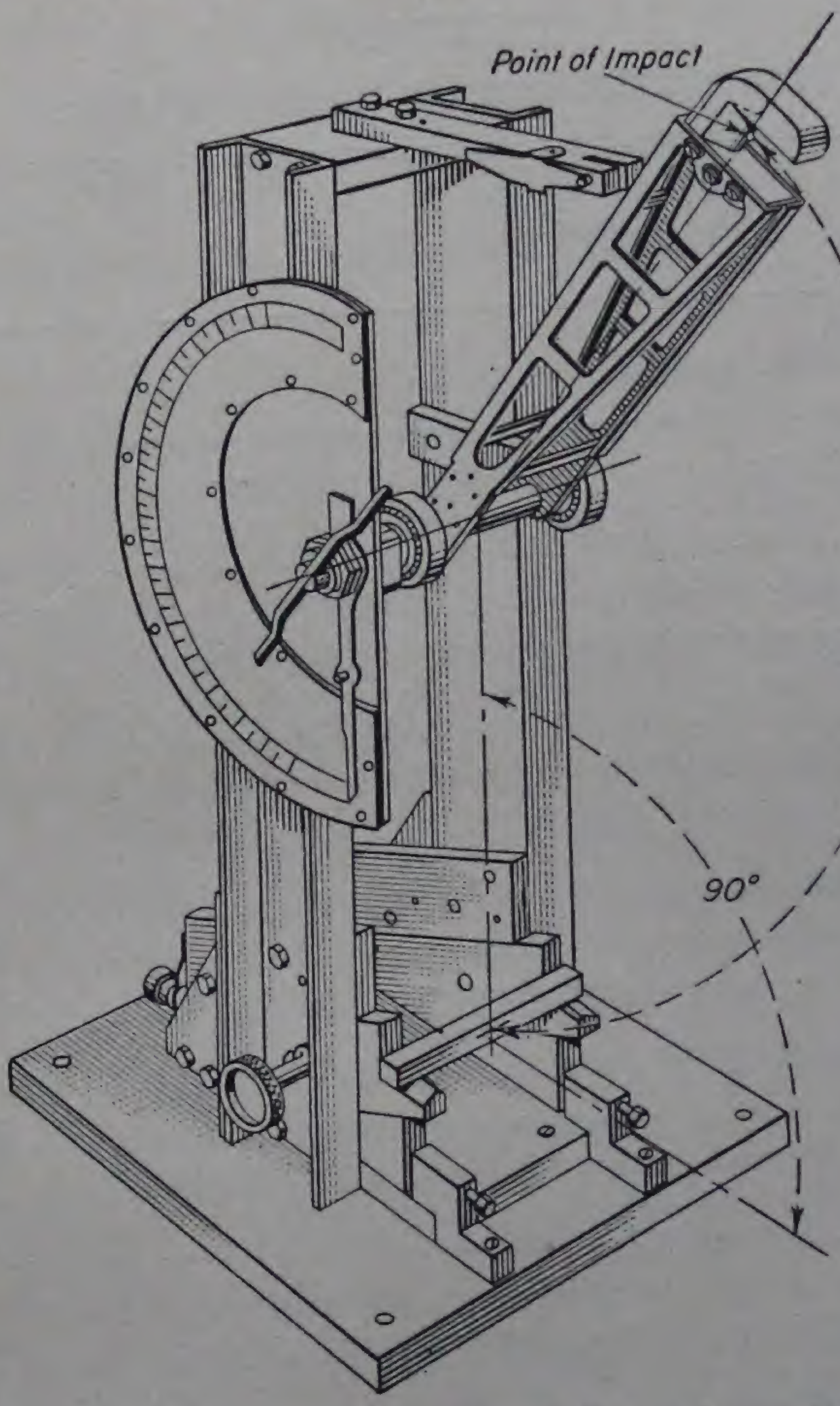


Fig. 11-13. Charpy-Type Simple-Beam Impact Machine.

In the Charpy machine, Fig. 11-13, the sample is set horizontally against two stops with the notch facing away from the pendulum. The sample is set so that the pendulum strikes it in the middle. The sample for the Charpy test is $\frac{1}{2}$ in.$\times\frac{1}{2}$ in.$\times$5 in. and the stop supports are set 4 inches apart.

11-31. Impact Strengths of Plastic Materials.—The preparation of the sample for the impact test is very important. If the material is thermosetting, the impact strength depends on the cure of the material and the density of the article. For example, resin-impregnated canvas is the best impact material among the common molding materials. The technique of molding it is to keep the temperature low enough so that the resin will not separate from the canvas, and to keep the pressure low enough so that the fabric

TABLE 11-9

IMPACT STRENGTHS OF VARIOUS PLASTICS

Material	Impact Strength Foot-Pounds per Inch of Notch
Phenol formaldehyde (molded)	
Transparent	.23–.40
General purpose	.20–.40
Heat resistant	.22–.72
Impact	.80–4.8
Phenol formaldehyde (laminated)	
Paper base	.60–.76
Cotton base	1.4–15.0
Asbestos base	1.8–11.0
Phenol formaldehyde (cast)	
No filler	.5–.6
Urea formaldehyde	.28–.32
Melamine formaldehyde	
Cotton filled	.26–.30
Asbestos filled	.28–.40
Cold molded	
Non-refractory	.3–.5
Refractory	.3–.5
Casein formaldehyde	.9–1.2
Shellac	2.6–2.9
Vinyl chloracetate	.4–1.2
Vinylidene chloride	2.0– .0
Methyl methacrylate	.2–.4
Polystyrene	.3–.5
Ethyl cellulose	.6–6.5
Cellulose acetate	.7–4.0
Cellulose acetobutyrate	.8–5.5
Cellulose nitrate	2.0–8.0
High acetyl cellulose acetate	.5–4.0

itself will not tear. If either of these two conditions is violated, the impact strength of the material is impaired.

Specimens are sometimes subjected to conditioning before testing. Great interest has recently been shown in the impact values of various materials at low temperatures. The samples used in sub-zero tests are conditioned at $-40°$ C for several hours, and are then tested as soon as possible after removal from the freezing chamber. The general impact results listed in publications are all for normal conditions. The average value of a series of tests is always used in determining the impact value for any material.

When standard samples are used in the Izod test, the energy required to break the sample is usually expressed as foot-pounds per inch of notch. The values given in Table 11-9 are the results of the Izod test. The values for a particular material represent the minimum and maximum values for various flows and formulas of the given plastic.

11-32. Hardness.—The hardness value for plastics is usually expressed in terms of surface indentation rather than as surface resistance to scratch. The Brinell and Rockwell methods are most commonly used to determine the hardness of plastic materials. Both methods are practically the same, but the measurement of the value is different. The tests consist in applying pressure to a steel ball resting against a flat surface of a plastic, which is supported on a firm foundation. The sample must be absolutely flat, as warpage interferes with the test. The Brinell method measures the spherical indentation caused by pressing a steel ball 10 millimeters in diameter into the test surface with a force of 500 or 3,000 kilograms. The average of two diameters of impression gives the diameter from which the hardness number is read from tables. By calculation, the hardness number is the force applied divided by the spherical area of the impression expressed in square millimeters. In order to obtain precision from a Brinell test, the surface indented should be horizontal, level, and smooth enough to have its diameter measured accurately by the scale in the Brinell microscope. There must be enough mass of material about the impression so that the piece as a whole does not deform and, by change of dimension, spread the diameter. Objects tested must also be thick enough to prevent the support from influencing the results.

The Rockwell method is similar to the Brinell method, but the amount of the force and the method of its application are different. A hardened steel ball or a diamond point is used as the penetrator, and the load is applied in two stages. The first, or minor, load is 10 kilograms, and the second, or major, load is 60 or 100 kilograms, the amount depending on the material tested. In addition, since plastic materials have a tendency to flow continuously under sustained uniform pressure, a time factor is also required; that is, the load application must be for a certain duration, as, for example, 8 or 10 seconds. The Rockwell method evaluates the hardness by pressing a suitable penetrator into the

TABLE 11-10

HARDNESS OF VARIOUS PLASTICS

Material	Rockwell Hardness
Phenol formaldehyde (molded)	
Transparent	M80–M130
General purpose	M100–M125
Heat resistant	M85–M120
Impact	M85–M110
Phenol formaldehyde (laminated)	
Paper base	M70–M120
Cotton base	M70–M120
Asbestos base	M70–M110
Phenol formaldehyde (cast)	
No filler	M65–M80
Urea formaldehyde	M110–M130
Melamine formaldehyde	
Cotton filled	
Asbestos filled	M110–M115
Cold molded	
Non-refractory	M35–M65
Refractory	M35–M65
Casein formaldehyde	M26–M30
Shellac	
Vinyl chloracetate	M60–M80
Vinylidene chloride	M50–M65
Methyl methacrylate	M60–M90
Polystyrene	M75–M90
Ethyl cellulose	M25–M65
Cellulose acetate	M25–M80
Cellulose acetobutyrate	M25–M75
Cellulose nitrate	M25–M60
High acetyl cellulose acetate	M25–M80

surface in question, and expresses the degree of penetration on an arbitrary inverse scale so that the higher scale reading indicates a harder surface. The hardness values are designated by a letter and a number. For phenolic-laminated sheets, a $\frac{1}{4}$-inch ball penetrator, a minor load of 10 kilograms, and a major load of 100 kilograms are used. This combination is known as the M scale. For vulcanized fiber, a $\frac{1}{2}$-inch ball penetrator, a minor load of 10 kilograms, and a major load of 60 kilograms are used. This combination is known as the R scale. The readings should always be recorded under their correct headings, the letter *M* preceding the hardness number for phenolic laminated sheets and the letter *R* preceding the hardness number for vulcanized rubber.

The hardness values listed in Table 11-10 are according to the Rockwell M scale. The values for a given material represent the minimum and maximum values for the various flows and formulas of the plastic.

11-33. Hardness Test for Rubbery Material.—It is almost impossible to test the hardness of a rubbery material by the Brinell or Rockwell method, because the elasticity of the material causes it to practically regain its normal shape; hence, the true indentation cannot be measured. The hardness of a rubbery material is usually measured by a penetration test, in which a needle penetrates the sample. The force required to make the penetration is a measure of the hardness of the material. Test samples, particularly those of thermosetting materials, are important in the determination of values. Care must be taken that the part is fully cured. If the test sample, for example, is a resin-impregnated rag material, the resin must not be allowed to separate from the rag. If this were to happen, the resin would flow to the top surface of the test sample, and the test would be performed on cured resin and not on a combination of rag and resin. The value resulting from such a test would not be indicative of the true hardness of the material.

Electrical Properties

11-34. Dielectric Strength.—One of the most important electrical properties of a plastic material is its dielectric strength, which may be defined as the voltage gradient at which electrical failure, or breakdown, occurs. It may be calculated by dividing the voltage by the thickness of the test sample between the electrodes. The dielectric-strength test is a comparative one, because the results are affected by such variables as the frequency of the voltage, the thickness of the test piece, the size and shape of the electrodes, the temperature, and the surrounding medium. Standard alternating current has a frequency of 60 cycles, that is, the current reverses its direction 60 times per second. Radio frequencies are in millions of cycles. The dielectric-strength test may be run at any frequency, and the dielectric strength is expressed as volts per mil. A mil is $\frac{1}{1000}$ inch.

The thickness of the molded sample is very important. It is generally found that thin samples will stand more volts per mil

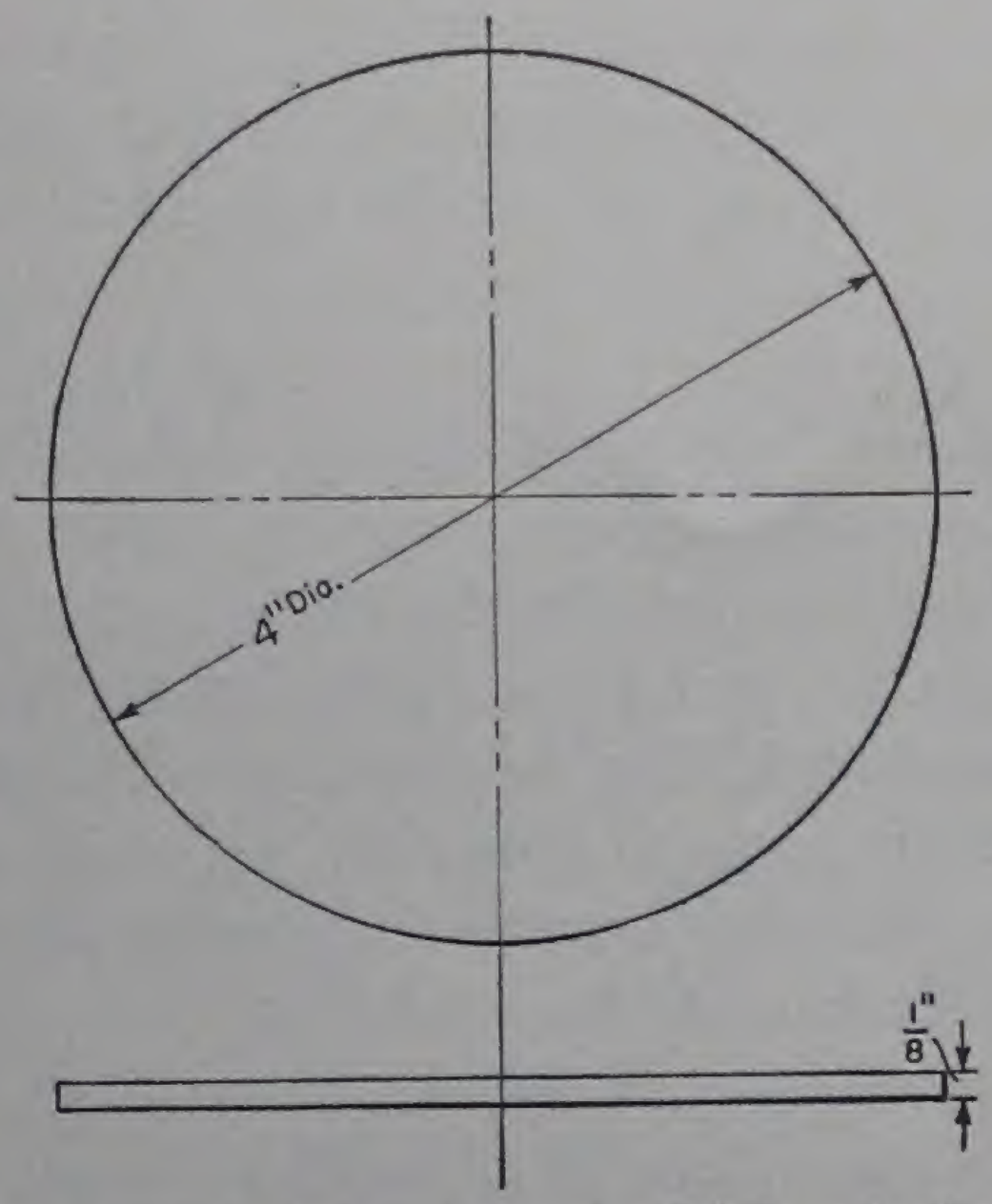


Fig. 11-14. Standard Specimen for Dielectric-Strength Test.

than thick samples. The standard test sample, as used in Specification 17P4(INT) of the Bureau of Ships, is shown in Fig. 11-14. The test pieces are molded disks about 4 inches in diameter and from $\frac{1}{8}$ to $\frac{1}{4}$ inch thick. The test is usually conducted at room temperature after the sample has been either immersed in water for 48 hours or held at some elevated temperature for a like period. The tests are usually conducted under oil, but may be conducted in air. In either case, the condition under which the test is conducted should be reported.

The three methods used for testing dielectric strength are: the short-time method, the step-by-step method, and the endurance method. The equipment is the same for all three methods, and the voltages required for the tests may run well over 100,000 volts. For voltages up to 50,000, a 2-kva (kilovolt-ampere) transformer is required; and, for voltages over 50,000, a 5-kva transformer is required. The test electrodes, which should be of brass or copper, are usually 2 inches in diameter and 1 inch long. The contacting surfaces should be highly polished, and the contact edges should have a $\frac{1}{8}$-inch radius. A voltmeter is connected directly into the system so as to measure the voltage passing through the electrodes.

11-35. Short-Time Method.—In the short-time method, the disk sample is set in an insulated ring and the two electrodes are

placed one on either side at the exact center of the sample. Starting at zero voltage, the load is increased uniformly at the rate of 500 volts per second until breakdown occurs. The number of volts required to cause the breakdown divided by the thickness of the sample gives the dielectric strength in volts per mil. The normal time allowed for breakdown should be approximately 40 seconds. When the test runs for more than 40 seconds, the increment, or rate of increase of the voltage, should be increased so that breakdown occurs in approximately 40 seconds. Should the sample break down in less than 40 seconds, the increment should be decreased so that breakdown occurs in approximately 40 seconds. A dozen tests should be made and the average value should be taken as the short-time dielectric strength.

11-36. **Step-by-Step Method.**—The principle of the step-by-step method is to increase the voltage by a definite amount over a definite period of time until breakdown occurs. Instead of starting at zero voltage, the initial voltage applied should be about 40 per cent of the breakdown voltage in the short-time test, adjusted as shown in Table 11-11. The voltage should then be increased by the equal increments given in the same table. The change from each step to the next higher should be made as rapidly as possible. The table lists the approximate voltage adjustments and increments for the various breakdown voltages, according to the Navy Specification 17P4 (INT).

TABLE 11-11

STEP-BY-STEP TEST, NAVY SPECIFICATION 17P4 (INT)

Breakdown Voltage by Short-Time Method Kilovolts	Initial Voltage Adjustment Kilovolts	Increment of Increase Kilovolts
12.5 or less	.5	.5
Over 12.5-25 inclusive	1.0	1.0
Over 25-50 inclusive	2.5	2.5
Over 50-100 inclusive	5.0	5.0
Over 100	10.0	10.0

EXAMPLE 1.—The breakdown voltage by the short-time method is 36 kilovolts. Determine the initial voltage and the second-step voltage in the step-by-step test.

SOLUTION.—40 per cent of breakdown voltage = 14.4 kilovolts.
Initial voltage obtained by adjustment to the nearest 2.5 kilovolts = 15.0 kilovolts.
Increment according to Table 11-11 = 2.5 kilovolts.
Second-step voltage would be 17.5 kilovolts.

The time usually allowed for the change from one voltage to the next is 10 seconds, and each individual voltage is applied for 1 minute. The step-by-step method is really an intermediate test between the short-time test and the endurance test. The test itself is over a variety of voltages, with some time allowed for breakdown at each phase or step. The fatigue factor is one of the reasons why the initial voltage is 40 per cent of the breakdown voltage. If the initial voltage were 500 or 1,000 volts and a 1-minute interval were allowed for each step, the sample would undergo severe strain and would probably break down before the true dielectric value had been reached. By starting with 40 per cent of the voltage, the strain is partially done away with.

The American Society for Testing Materials (A.S.T.M.) uses 50 per cent for the initial voltage in the step-by-step test. The voltage-adjustment figure also differs from the Navy Specification figure. It is this adjustment differential that makes up for the difference in the initial voltage. The A.S.T.M. adjustments are listed in Table 11-12.

TABLE 11-12

STEP-BY-STEP TEST, A.S.T.M. SPECIFICATIONS

Breakdown Voltage by Short-Time Method Kilovolts	Initial Voltage Adjustment Kilovolts	Increment of Increase Kilovolts
25 or less	1.0	1.0
Over 25-50 inclusive	2.0	2.0
Over 50-100 inclusive	5.0	5.0
Over 100	10.0	10.0

EXAMPLE 2.—Solve Example 1 by using the A.S.T.M. Specifications.
SOLUTION.—50 per cent of breakdown voltage = 18.0 kilovolts.
Initial voltage obtained by adjusting to nearest 2.0 kilovolts = 18 kilovolts.
Second-step voltage would be 20 kilovolts.

11-37. Endurance Method.—The endurance method of test is quite different from the short-time method of test, as it maintains a definite voltage for a definite period of time. Its principle is the same as that of the short-time method, but the voltages are much lower initially and the length of each testing step is much longer. The initial voltage is 10 per cent of the short-time breakdown strength, and the time allowed at each step is 30 minutes. The

increment is 20 per cent of the initial voltage, and the test is continued until the sample breaks down.

The test report should contain both the breakdown voltage and the length of time required for the complete test. Although two materials may break down at the same voltage, it is possible that the length of time at the particular voltage may vary. For example, two samples having the same starting voltage and the same increment are tested. The starting voltage may be 5 kilovolts, and the increment 1 kilovolt. One sample withstands breakdown for 1 hour and 5 minutes, the other for 1 hour and 25 minutes. Although both samples break down under the 7-kilovolt load, it is obvious that one sample must be superior to the other. The time differential, as well as the load or voltage applied, is a measurement for comparing two materials. The endurance method was set up as a time test rather than a voltage measurement, and is designed to reveal the ability of plastic materials to resist electrical stress at elevated temperatures. The endurance test is usually marked by an increase in temperature, which should be reported.

11-38. Dielectric Strengths of Plastic Materials.—The dielectric-strength values of plastic materials are usually given for the short-time and the step-by-step methods, but not for the endurance method. The values listed in Table 11-13 are expressed as volts per mil.

11-39. Dielectric Constant.—The dielectric constant of a material is a measure of the electrostatic energy that the material is capable of storing per unit potential. The dielectric constant, or inductive capacitance, of a material is equal to the ratio of the capacitance of a condenser with the given substance as the dielectric to the capacitance of the same condenser with air or a vacuum as the dielectric. A condenser, which is electrically rated by its capacitance, results when two conducting materials are separated from each other by a dielectric material. The dielectric constant of air is 1.

Several factors, one of which is the frequency at which the observations are made, influence the dielectric constant. For this reason, the usual practice is to tabulate the dielectric constant of an insulating plastic at 60, at 10^3 (or 1,000), and at 10^6 (or 1,000,000) cycles. Typical values for various flows and formulas of a particular plastic are listed in Table 11-14. Dielectric constants of some

TABLE 11-13

DIELECTRIC STRENGTHS OF VARIOUS PLASTICS

Material	Volts per Mil, $\frac{1}{8}$ Inch Thickness	
	Short-Time Test	Step-by-Step Test
Phenol formaldehyde (molded)		
Transparent	400–500	250–350
General purpose	300–500	200–350
Heat resistant	250–400	200–400
Impact	150–450	100–350
Phenol formaldehyde (laminated)		
Paper base	400–1,000	250–600
Cotton base	150–600	150–400
Asbestos base	60–150	50–125
Phenol formaldehyde (cast)		
No filler	350–430	260–335
Urea formaldehyde	650–720	300–380
Melamine formaldehyde		
Cotton filled	340–350	380–410
Asbestos filled		310–330
Cold molded		
Non-refractory	70–90	50–75
Refractory		50–75
Casein formaldehyde	400–700	
Shellac	200–600	
Vinyl chloracetate	380–410	360–380
Vinylidene chloride	500	340
Methyl methacrylate	500	400
Polystyrene	500–700	450–600
Ethyl cellulose	400–700	
Cellulose acetate	290–600	200–300
Cellulose acetobutyrate	250–400	
Cellulose nitrate	300–600	250–550
High acetyl cellulose acetate	290–600	200–300

phenolic plastics are affected by temperature changes, some constants having been known to change as much as 20 per cent as the temperature increased from 25° to 90° C. Water also affects the dielectric constant. The dielectric constants of phenolic plastics increase after a 24-hour water immersion.

11-40. **Power Factor.**—Power factor is technically defined as the cosine of the dielectric phase angle or the sine of the dielectric loss angle. In clearer terms, power factor is the measurement of leakage of power through a dielectric material. *Dielectric phase angle* is the angular difference in phase between the sinusoidal

TABLE 11-14

DIELECTRIC CONSTANTS OF VARIOUS PLASTICS

Material	60 Cycles	10^3 Cycles	10^6 Cycles
Phenol formaldehyde (molded)			
Transparent	5.0–6.5	4.5–6.0	4.5–5.0
General purpose	7.5–15.0	6.0–9.5	5.0–6.8
Heat resistant	35.0–50.0	20.0–30.0	6.5–8.0
Impact	5.7–9.0	5.5–6.7	4.7–5.2
Phenol formaldehyde (laminated)			
Paper base			3.6–5.5
Cotton base			4.5–7.0
Asbestos base			
Phenol formaldehyde (cast)			
No filler	5.0–5.5	5.0–5.5	4.7–4.9
Urea formaldehyde	7.0–9.5	6.4–9.0	6.3–7.5
Melamine formaldehyde			
Cotton filled	7.5–8.3		6.7–7.3
Asbestos filled	6.4–9.9		6.7
Cold molded			
Non-refractory	15.0		6.0
Refractory			6.1–6.8
Casein formaldehyde	3.0–4.0	4.0–5.0	
Shellac	3.26	3.21	3.08
Vinyl chloracetate	3.0–5.0	3.0–5.0	3.0–5.0
Vinylidene chloride	3.0–3.7	3.0–3.5	2.8–3.3
Methyl methacrylate	2.5–2.7	2.5–2.7	2.5–2.7
Polystyrene	3.1–3.3	3.0–3.8	3.2–3.7
Ethyl cellulose	3.5–6.4	3.5–6.4	3.2–6.2
Cellulose acetate	3.5–6.4	3.5–6.4	3.2–6.2
Cellulose acetobutyrate	6.7–7.3		6.2
Cellulose nitrate	3.5–6.4	3.5–6.4	3.2–6.2
High acetyl cellulose acetate			

voltage applied to the dielectric and the component of the resulting current which has the same frequency as the applied voltage. *Dielectric loss angle* is the difference between 90 electrical degrees (90°) and the dielectric phase angle. At high frequencies, such as radio frequencies, the power leakage is a very important factor. The power factor of a material varies with the frequency of the current. The values listed in Table 11-15 for 60, 10^3, and 10^6 cycles cover a variety of flows and formulas for each plastic.

11-41. Arc Resistance.—Plastics are often used as electrical insulators under conditions where arcing may result. For such cases, ureas are very good and phenolics, unless specially prepared

TABLE 11-15

POWER FACTORS OF VARIOUS PLASTICS

Material	60 Cycles	10^3 Cycles	10^6 Cycles
Phenol formaldehyde (molded)			
Transparent	.06–.10	.03–.08	.015–.03
General purpose	.25–.50	.07–.25	.04–.06
Heat resistant	.25–.45	.17–.35	.12–.15
Impact	.06–.35	.03–.15	.03–.05
Phenol formaldehyde (laminated)			
Paper base			
Cotton base			
Asbestos base			
Phenol formaldehyde (cast)			
No filler	.10–.15	.01–.05	.02–.08
Urea formaldehyde	.035–.10	.035–.05	.027–.04
Melamine formaldehyde			
Cotton filled	.025–.050		.023–.029
Asbestos filled	.07–.17		.041
Cold molded			
Non-refractory	.02		.07
Refractory			
Casein formaldehyde			.052
Shellac	.004–.04	.05	
Vinyl chloracetate	.008	.01	.014
Vinylidene chloride	.03–.08	.03–.15	.03–.05
Methyl methacrylate	.05–.06	.06–.07	.02–.03
Polystyrene	.0001–.0003	.0001–.0003	.0001–.0003
Ethyl cellulose	.007	.008–.015	.001–.02
Cellulose acetate	.01–.06	.01–.06	.01–.05
Cellulose acetobutyrate	.01–.04	.01–.04	.01–.04
Cellulose nitrate	.06–.15		.07–.10
High acetyl cellulose acetate	.01–.06	.01–.06	.01–.05

for arc resisting, are poor. The test for arc resistance is a surface test, which is conducted by drawing a high-voltage, low-current a-c arc between two tungsten-pointed electrodes, Fig. 11-15, that rest on the surface of the material under test. The principle of the test is to find the time required to make the material become a conductor, or, as the term is commonly used, "track arc." The results are usually reported in milliamperes per second. A milliammeter is connected in the circuit along with the source of energy, which is a high-voltage transformer.

The current is set at 10 milliamperes, and the circuit is closed for 60 seconds. A bright arc will flash continuously across the electrodes. The current is increased to 20 milliamperes for 60

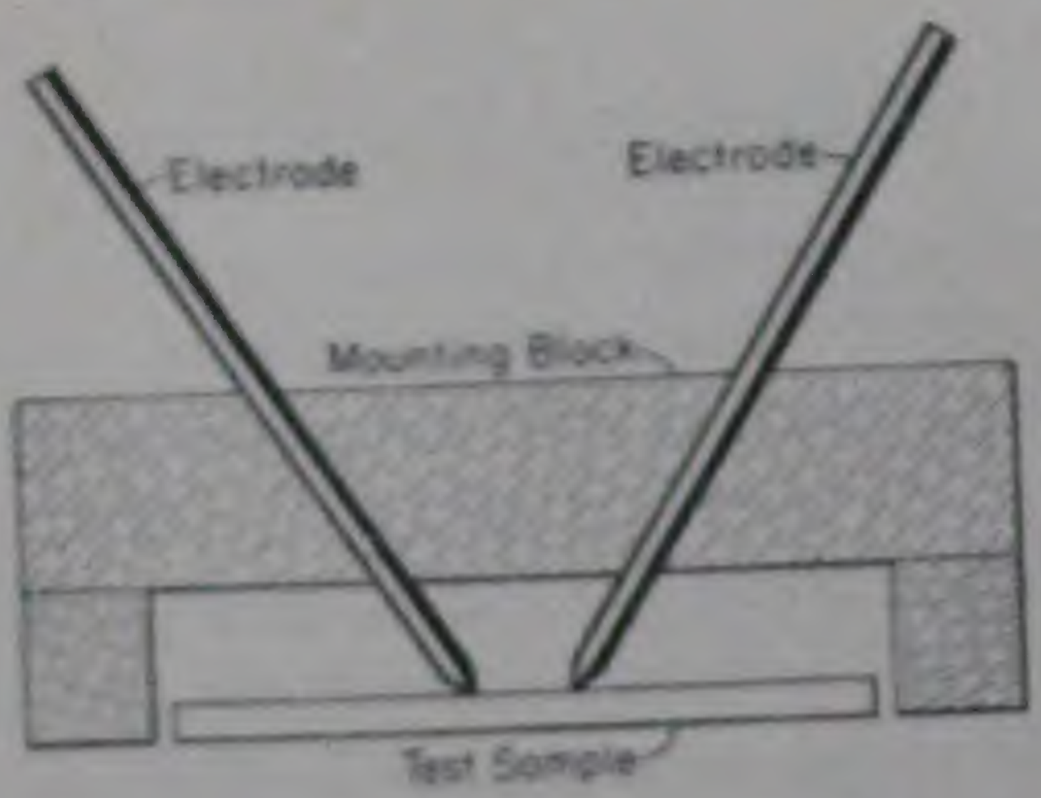


Fig. 11-15. Apparatus for Arc Resistance Test.

seconds. The increment, therefore, is 10 milliamperes and the time is 60 seconds. This procedure is followed until the material fails by conducting the current. The material becomes conducting when the arc ceases to travel through the air but travels over the surface of the material. The arc changes from a bright color to a dull yellow burning color. The current step and the time in that step when the color of the arc changes are the important facts for the record.

The sample should be thoroughly examined after the test for carbonization, fusing, or melting. Phenol plastics in particular will carbonize across the surface in the presence of an electric arc, forming a conducting surface. Acrylic plastics and shellac are reported to be particularly good under arcing conditions and will not tend to "track" across the surface.

The test should be discontinued when 100 milliamperes is reached, as the electrodes burn out rapidly at that high current. In some cases, where materials have a low arc resistance, a more accurate value is obtained by using an interrupter, which eliminates the strain of a steady 10-milliampere current. The interrupter flashes the 10 milliamperes on and off at regular intervals until the material is gradually made ready for the tests. Typical interrupter cycles are set for $\frac{1}{4}$ second on and $1\frac{3}{4}$ seconds off for the first 60-second step. This is gradually changed to $\frac{1}{4}$ second on and $\frac{1}{8}$ second off over a 60-second interval.

Chemical Properties

11-42. Effects of Acids.—Acids are one of the greatest chemical enemies of metals. Since many plastics have superior acid-resisting qualities, they have replaced metal in many applications. Different kinds of acids have different effects, and so three types of acids are used for testing: weak or dilute acid, strong or concentrated acid, and oxidizing acid. A 5% or 10% solution of hydrochloric acid serves as an example of a dilute acid, a 35 to 39% solution of the same acid represents a strong acid, and chromic acid may be regarded as an oxidizing acid.

The molded sample used in the determination of the effect of acids is of extreme importance, particularly where thermosetting materials are involved. If the sample has not been fully cured, some portion of the binder will be soluble or fusible and will be subject to attack. With thermoplastics, this is not the case, since the chemical composition does not undergo any change during molding.

The usual procedure for testing a plastic material for the effects of acids is simply to place a molded sample in a beaker containing the particular type of acid. The length of time the sample is kept in the acid is left to the discretion of the tester. The sample is examined periodically to see what the effect of the acid has been. There are many ways in which the sample may be attacked. The most obvious is the direct disintegration of the sample. Other factors that must be noted are the degree of crazing, or cracking, the loss of surface luster, and bloating due to absorption.

There is no standard method for reporting the effect of acids on the plastic, other than noting anything that may happen to the plastic and the time at which it starts to happen. If an acid has an effect on the plastic material, the test should not be stopped at the first sign of an effect. The test should be continued, and the increase in effect with the increase of time should be noted. In many cases it will be found that a material will be slightly attacked in the first 24 hours, but will not be attacked by any further testing. The samples should be examined once every 24 hours until an effect is noticed. When an effect is noticed, the sample should be examined at more frequent intervals.

In addition to the three types of acids used in ordinary tests, it may be necessary to use other acids when a plastic material is

TABLE 11-16

EFFECTS OF ACIDS ON VARIOUS PLASTICS

Material	Oxidizing Acid	Weak Acid	Strong Acid
Phenol formaldehyde (molded)			
Transparent	Decomposes	None to slight	None to slight
General purpose	Decomposes	None to slight	None to slight
Heat resistant	Decomposes	None to slight	None to slight
Impact	Decomposes	None to slight	None to slight
Phenol formaldehyde (laminated)			
Paper base	Decomposes	None to slight	None to slight
Cotton base	Decomposes	None to slight	None to slight
Asbestos base	Decomposes	None to slight	None to slight
Phenol formaldehyde (cast)			
No filler	Decomposes	None to slight	None to slight
Urea formaldehyde	Decomposes	None to slight	Decomposes
Melamine formaldehyde			
Cotton filled	Decomposes	None	Decomposes
Asbestos filled	Decomposes	None	Decomposes
Cold molded			
Non-refractory	Decomposes	Slight	Decomposes
Refractory	Decomposes	Slight	Decomposes
Casein formaldehyde	Decomposes	Very slight	Decomposes
Shellac	Decomposes	Deteriorates	Decomposes
Vinyl chloracetate	None	None	None
Vinylidene chloride	Very slight	None	Very slight
Methyl methacrylate	Marked	None	None
olystyrene	Marked	None	None
Ethyl cellulose	Decomposes	Slight	Decomposes
Cellulose acetate	Decomposes	Slight	Decomposes
Cellulose acetobutyrate	Decomposes	Slight	Decomposes
Cellulose nitrate	Decomposes	Slight	Decomposes
High acetyl cellulose acetate	Decomposes	Slight	Decomposes

tested for a special application. Hydrofluoric acid, for instance, could be stored only in paraffin bottles until the introduction of plastics that were not affected by that acid. When a plastic is to be tested for its resistance to a special acid, the test should be run with the acid itself.

11-43. Acid-Resistant Properties of Plastic Materials.—Although it has been stated that there are three types of acids, the distinction between these types is not clear cut. Thus, in certain cases it may be difficult to say whether an acid is a weak strong acid or a strong weak acid. The effect of an acid on a soft-flow material might be entirely different from the effect of the same

acid on a hard-flow material of the same kind. The effects of acids on various plastic materials are indicated in a general way in Table 11-16. Values for acid effects cannot be given numerically; so they are described in words. The best procedure is to test the specimen under actual conditions required by the proposed application.

11-44. Effects of Alkalies.—The alkalies are classed in two groups, the weak and the strong. Dilute solutions of calcium or barium hydroxide are examples of weak alkalies, and concentrated solutions of sodium or potassium hydroxide are examples of strong alkalies. The procedure for the test is the same as that described for acids. The tests for alkali resistance are, as a rule, run in conjunction with the acid tests. The effects of alkalies on various plastic materials are shown in Table 11-17.

11-45. Effects of Solvents.—Plastic stirrers frequently come into contact with alcohol; motor and engine parts frequently come into contact with oils and greases; and plastic bottle caps and dispensers are in direct contact with many types of liquids that are classed under the general name of solvents. Therefore, it is important that the molder pick the material which he knows will stand up under the particular solvent in use in the application.

The list of solvents is almost endless, and in most cases the plastic materials are tested for individual solvents rather than groups of solvents. The group method does, however, have some use and value in testing. Ethyl alcohol and butyl alcohol are both members of the alcohol family. Any plastic that will resist ethyl alcohol will resist butyl alcohol, but the reverse is not true. To test a plastic for alcohol resistance would mean testing for several hundred alcohols and, since this is not practical, the group method is used. The number of chain carbons is the determining factor. Ethyl alcohol has two carbons and butyl alcohol has four carbons. It seems that the lower the number of carbons, the more reactive the alcohol. Methyl alcohol is more destructive than ethyl alcohol, and octyl alcohol is less reactive than butyl alcohol. The same is generally true for ketones, esters, ethers, hydrocarbons, and chlorinated hydrocarbons. The usual testing materials are ethyl acetate for the ester family, acetone for the ketone family, ethyl methyl ether for the ether family, toluene or hexane for the hydro-

TABLE 11-17

EFFECTS OF ALKALIES ON VARIOUS PLASTICS

Material	Weak Alkali	Strong Alkali
Phenol formaldehyde (molded)		
Transparent	Slight to marked	Decomposes
General purpose	Slight to marked	Decomposes
Heat resistant	Slight to marked	Decomposes
Impact	Slight to marked	Decomposes
Phenol formaldehyde (laminated)		
Paper base	Slight to marked	Decomposes
Cotton base	Slight to marked	Decomposes
Asbestos base	Slight to marked	Decomposes
Phenol formaldehyde (cast)		
No filler	Slight to marked	Decomposes
Urea formaldehyde	Slight to marked	Decomposes
Melamine formaldehyde		
Cotton filled	None	None
Asbestos filled	None	None
Cold molded		
Non-refractory	None	Decomposes
Refractory	None	None
Casein formaldehyde	Softens	Decomposes
Shellac	Deteriorates	Deteriorates
Vinyl chloracetate	None	None
Vinylidene chloride	None	None
Methyl methacrylate	None	None
Polystyrene	None	None
Ethyl cellulose	None	None
Cellulose acetate	Slight	Decomposes
Cellulose acetobutyrate	Slight	Decomposes
Cellulose nitrate	Slight	Decomposes
High acetyl cellulose acetate	Slight	Decomposes

carbon family, and carbon tetrachloride for the chlorinated hydrocarbon family.

The actual test for effects of a solvent is the same as for an acid or an alkali; namely, the test sample is placed in a beaker with the test solvent. The time and temperature are variables. As a rule the samples are weighed before the test is started and again at the conclusion of the test. The safest procedure is to test the plastic with the particular solvent in question under the conditions required by the application. Any change in weight may be taken as an attack by the solvent. A gain indicates chemical absorption by the plastic, and a loss indicates extraction of soluble matter by the solvent. The surface conditions, such as crazing and

TABLE 11-18

EFFECTS OF SOLVENTS ON VARIOUS PLASTICS

Material	Alcohols	Ketones	Ethers	Esters	Hydrocarbons		Chlorinated Hydrocarbons
					Aliphatic	Aromatic	
Phenol formaldehyde (molded)							
Transparent	None	None	None	None	None	None	None
General purpose	None	None	None	None	None	None	None
Heat resistant	None	None	None	None	None	None	None
Impact	None	None	None	None	None	None	None
Phenol formaldehyde (laminated)							
Paper base	None	None	None	None	None	None	None
Cotton base	None	None	None	None	None	None	None
Asbestos base	None	None	None	None	None	None	None
Phenol formaldehyde (cast)							
No filler	None	None	None	None	None	Slightly soluble	Slightly soluble
Urea formaldehyde	None	None	None	None	None	None	None
Melamine formaldehyde							
Cotton filled	None	None	None	None	None	None	None
Asbestos filled	None	None	None	None	None	None	None
Cold molded							
Non-refractory	None	None	None	None	None	None	None
Refractory	None	None	None	None	None	None	None
Casein formaldehyde	Slightly soluble	Slightly soluble	None	None	None	None	None
Shellac	Slightly soluble	Slightly soluble	Slightly soluble	Slightly soluble	None	Slightly soluble	Slightly soluble
Vinyl chloracetate	None	Soluble	Soluble	Soluble	None	Bloats	Bloats
Vinylidene chloride	None	Attacked	Soluble	Very soluble	None	Slightly soluble	Slightly soluble
Methyl methacrylate	None	Attacked	None	Very soluble	None	Very soluble	Very soluble
Polystyrene	None	Attacked	Soluble	Soluble	None	Very soluble	Very soluble
Ethyl cellulose	Bloats	Bloats	Bloats	Bloats	Bloats	Bloats	Bloats
Cellulose acetate	Bloats	Soluble	Slightly soluble	Soluble	Slightly soluble	Slightly soluble	Slightly soluble
Cellulose acetobutyrate	Bloats	Soluble	Slightly soluble	Soluble	Slightly soluble	Slightly soluble	Slightly soluble
Cellulose nitrate	Bloats	Soluble	Soluble	Soluble	Slightly soluble	Slightly soluble	Slightly soluble
High acetyl cellulose acetate	Bloats	Soluble	Slightly soluble	Soluble	Slightly soluble	Slightly soluble	Slightly soluble

TABLE 11-19

WATER ABSORPTION OF VARIOUS PLASTICS

Material	Absorption in 24 Hours Per Cent
Phenol formaldehyde (molded)	
Transparent	.1–.2
General purpose	.2–.6
Heat resistant	.01–.3
Impact	.5–2.5
Phenol formaldehyde (laminated)	
Paper base	.3–9.0
Cotton base	.3–9.0
Asbestos base	.3–2.0
Phenol formaldehyde (cast)	
No filler	.02–.05
Urea formaldehyde	1.0–3.0
Melamine formaldehyde	
Cotton filled	1.0–1.7
Asbestos filled	.08–.14
Cold molded	
Non-refractory	.6–2.0
Refractory	.5–15.0
Casein formaldehyde	7.0–14.0
Shellac	.4–.9
Vinyl chloracetate	.05–.15
Vinylidene chloride	.00–.01
Methyl methacrylate	.4–.5
Polystyrene	.00–.01
Ethyl cellulose	1.0–2.0
Cellulose acetate	2.0–4.5
Cellulose acetobutyrate	1.6–2.1
Cellulose nitrate	.6–2.0
High acetyl cellulose acetate	.9–2.5

loss of luster, should also be noted. The effects of solvents on various plastic materials are shown in Table 11-18.

11-46. Water Absorption.—Water absorption, as the name implies, is the susceptibility of the plastic material to absorb water upon immersion for a definite period. Whenever a plastic material is tested for alkali, acid, and solvent resistance, a check test must be made. The check consists in placing the plastic sample in a beaker containing freshly distilled water. The sample is weighed before immersion. On removal of the sample from the water, it is dried with a clean cloth and immediately weighed. The gain in weight is reported as water absorption With the exception of some

TABLE 11-20

COLOR POSSIBILITIES OF VARIOUS PLASTICS

Material	Type	Colors
Phenol formaldehyde (molded)		
Transparent	Transparent	Amber and dark shades
General purpose	Opaque	Dark shades
Heat resistant	Opaque	Dark shades
Impact	Opaque	Dark shades and natural
Phenol formaldehyde (laminated)		
Paper base	Opaque	Dark shades
Cotton base	Opaque	
Asbestos base	Opaque	
Phenol formaldehyde (cast)		
No filler	Translucent	Unlimited
	Opaque	
	Transparent	
Urea formaldehyde	Translucent	
	Opaque	
Melamine formaldehyde		
Cotton filled	Translucent	
	Opaque	
Asbestos filled	Opaque	Brown and dark shades
Cold molded		
Non-refractory	Opaque	Dark shades
Refractory	Opaque	Dark shades
Casein formaldehyde	Translucent	Unlimited
	Opaque	
Shellac	Opaque	
Vinyl chloracetate	Translucent	
	Opaque	
	Transparent	
Vinylidene chloride	Translucent	
	Opaque	
	Transparent	
Methyl methacrylate	Translucent	
	Opaque	
	Transparent	
Polystyrene	Translucent	
	Opaque	
	Transparent	
Ethyl cellulose	Translucent	
	Opaque	
	Transparent	
Cellulose acetate	Translucent	
	Opaque	
	Transparent	
Cellulose acetobutyrate	Translucent	
	Opaque	
	Transparent	
Cellulose nitrate	Translucent	
	Opaque	
	Transparent	
High acetyl cellulose acetate	Translucent	
	Opaque	
	Transparent	

vinyls, all plastics have a positive water absorption. The absorption never interferes with the surface characteristics of the material. It is the exception, rather than the rule, if cracking occurs because of moisture. In checking the effect of dilute acids and alkalies, the straight moisture factor must be taken into consideration. If an increase in weight is noticed with a dilute acid or alkali, it is entirely possible that the increase represents the moisture absorption of the material and not the chemical effect of the acid or the alkali.

The water-absorption values listed in Table 11-19 represent the per cent of weight increase during a 24-hour immersion period. The values for a particular plastic represent the minimum and maximum values for the various flows and formulas of the material.

11-47. Color Possibilities.—Some plastics are limited in their color range because certain fillers or types of raw materials are used in their manufacture. Some plastics are limited in their color range in the case of the opaque types only. Other plastics are unlimited in color range and type of color penetration. Table 11-20 illustrates the color limitations of the various plastic materials.

Thermal Properties

11-48. Distortion Under Heat.—Distortion under heat should not be mistaken as a test of the heat resistance of the material. It is the measurement of the amount of heat a material can withstand under stress without showing distortion. Resistance to heat should be construed to mean continuous heat. It is entirely possible that a material may have a heat resistance of 350° F, and yet show a distortion under stress at a temperature of only 285° F. The test, as shown in Fig. 11-16, places the material under stress at various temperatures. The load and the rate of temperature rise are the most important factors in the test.

The test as prescribed by the American Society for Testing Materials is as follows: The sample, in the condition received, is placed on two supports in the center of an air chamber. The supports are 4 inches apart, and the air chamber is entirely surrounded by oil. With such a set-up the temperature in the air chamber may be very accurately controlled. The starting temperature is 25° ± 2° C (77° ± 3.6° F), and the oil is heated gradually at a rate not to exceed 1° C every 2 minutes.

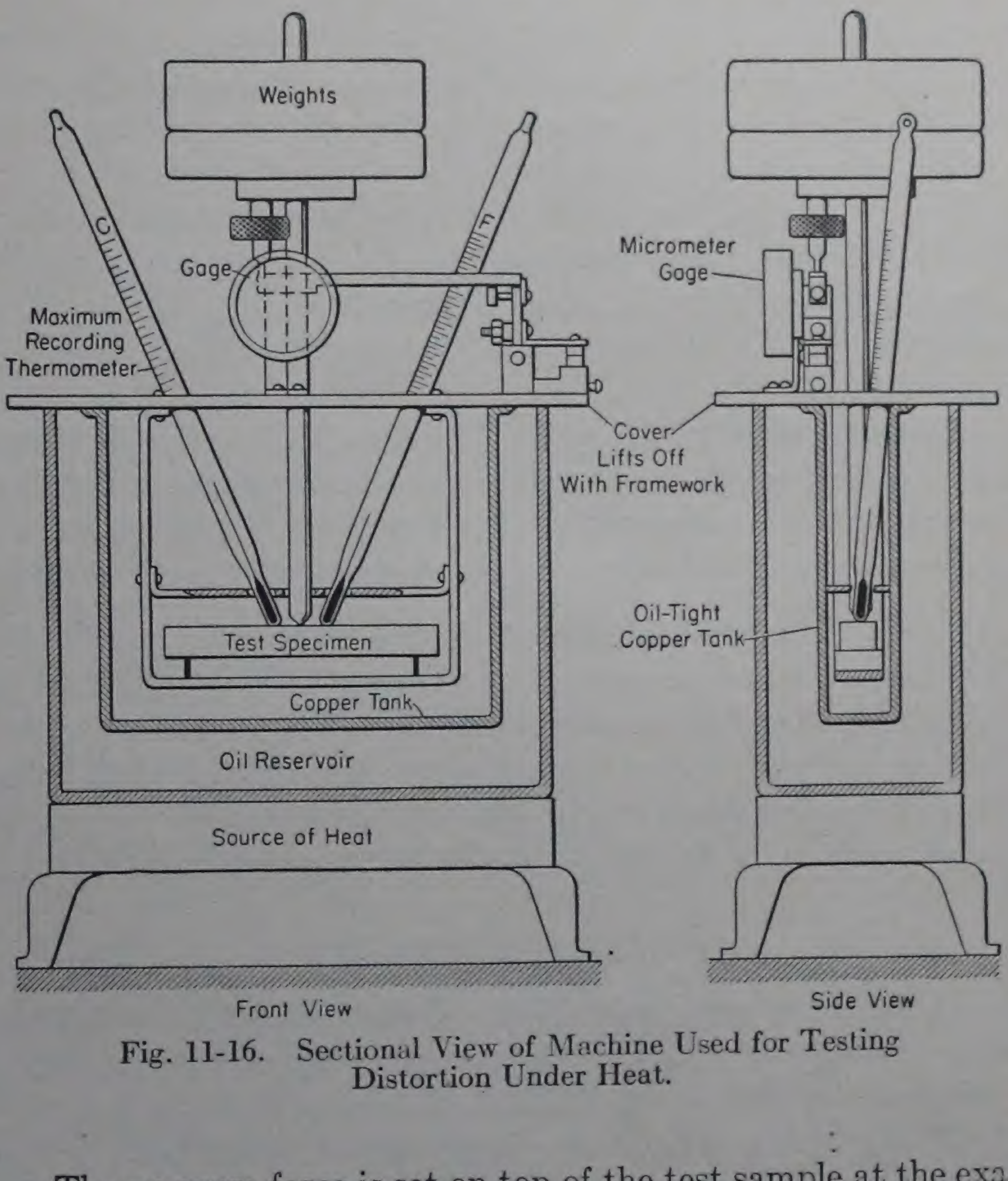


Fig. 11-16. Sectional View of Machine Used for Testing Distortion Under Heat.

The pressure force is set on top of the test sample at the exact mid-point, and a load of $5\frac{1}{2}$ pounds is applied. The apparatus has a scale graduated in thousandths of an inch to measure the actual deflection caused by the distortion of the sample. The thermometers are set directly in contact with the sample so as to record the temperature of the sample at any time during the test. The distortion point is the temperature at which the sample shows a deflection of .010 inch (10 mils) at the center between the supports.

The facts to be reported are the dimensions of the test sample, the temperature at which the 10-mil distortion occurs, the length of time required to reach the distortion point, and the condition of the specimen after the test. The average result of three such tests is considered to be the value for distortion under heat, but, if there is a great variance in any of the three values, additional

TABLE 11-21

THERMAL PROPERTIES OF VARIOUS PLASTICS

Material	Resistance to Heat Degrees F Continuous	Distortion Under Heat Degrees F
Phenol formaldehyde (molded)		
Transparent	250	240 -260
General purpose	300–310	270–285
Heat resistant	400–450	240–260
Impact	230	240–280
Phenol formaldehyde (laminated)		
Paper base	210–250	320–340
Cotton base	210–250	320–350
Asbestos base	250–300	320–350
Phenol formaldehyde (cast)		
No filler	160	140–175
Urea formaldehyde	180	260–280
Melamine formaldehyde		
Cotton filled	210	385
Asbestos filled	300–400	240–260
Cold molded		
Non-refractory	500	
Refractory	1,300	
Casein formaldehyde	300–325	300
Shellac	150–190	140–160
Vinyl chloracetate	130	140–150
Vinylidene chloride	160–200	150–180
Methyl methacrylate	120–140	125–160
Polystyrene	150–170	165–190
Ethyl cellulose	140–200	120–200
Cellulose acetate	140–190	140–200
Cellulose acetobutyrate	140–220	115–215
Cellulose nitrate	120	110–140
High acetyl cellulose acetate	150–200	130–220

samples should be tested. Values for resistance to heat and distortion under heat of various plastics are given in Table 11-21.

11-49. Coefficient of Thermal Expansion.—The coefficient of thermal expansion becomes increasingly important when plastics and metals are used in a single application. Like metals, all plastic materials undergo a change in dimension with any change in temperature. This property should not be confused with ordinary shrinkage. When a metal is used in combination with a plastic material, the coefficients of thermal expansion of both the metal

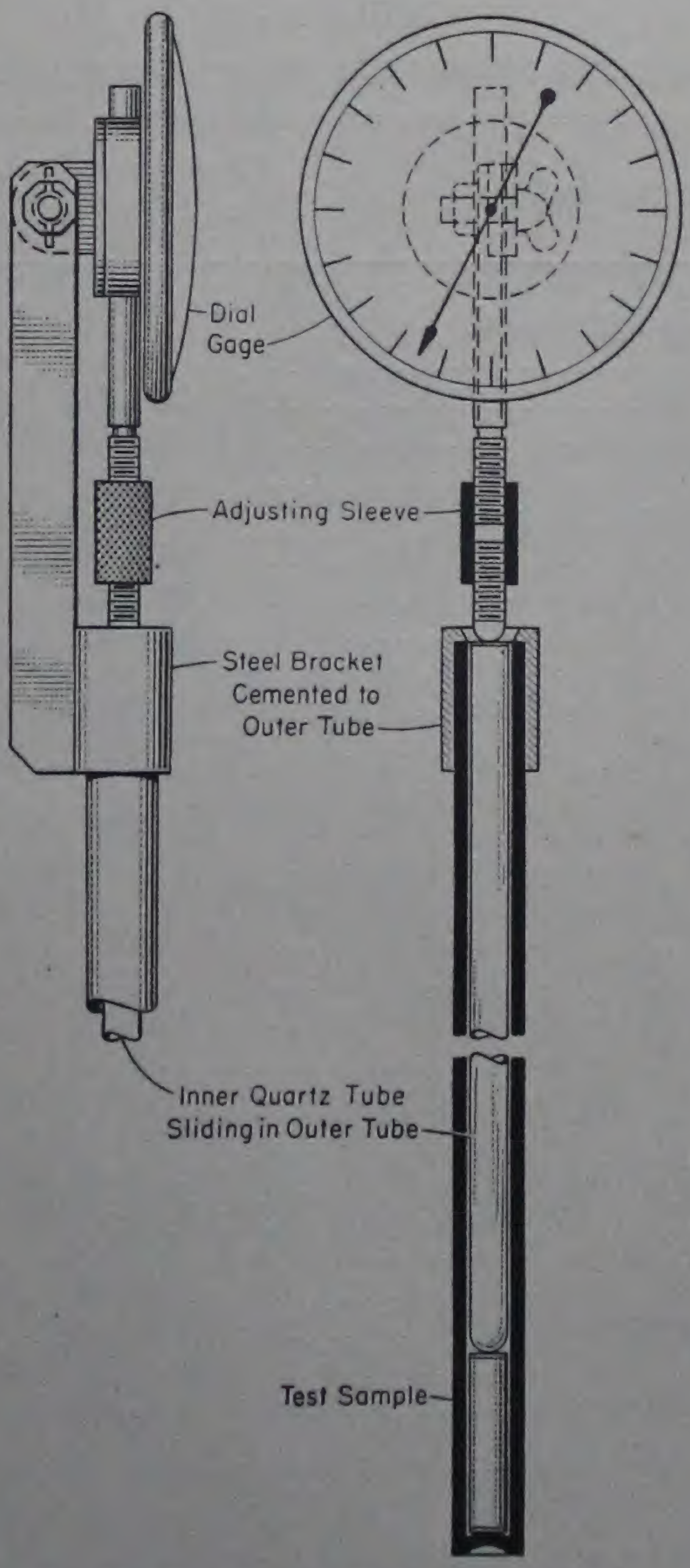


Fig. 11-17. Quartz-Tube Dilatometer.

and the plastic material must be carefully studied. The coefficient of thermal expansion, which is also referred to as thermal expansivity, may be defined as the change in inch per inch of material for each degree of Centigrade temperature change. The test to measure thermal expansion is a direct measurement test. It may be conducted by using a dilatometer, as shown in Fig. 11-17. The sample is placed inside the fused quartz tube, and the inner quartz tube is lightly placed on the sample, which rests on the bottom of

the main tube. The push finger connected to the dial is set by means of an adjustable sleeve on top of the inner quartz tube.

The test is started by first setting the gage at zero and then placing the whole apparatus, which contains the specimen, in a liquid bath having a temperature of −30° C. The temperature of the bath shall be maintained at −30° C until the specimen acquires the same temperature. The time required for the specimen to reach the bath temperature shall be determined by preliminary thermometer and stop-watch readings, because the dilatometer does not indicate when the specimen reaches the correct temperature. When the specimen has reached the bath temperature, −30° C, the reading of the gage is observed. The whole apparatus is then removed from the bath and is placed in another bath, having a temperature of 30° C. The expansion for this temperature is determined by repeating the procedure for the −30° C determination. The whole apparatus is then removed from the 30° C bath and returned to the −30° C bath. The gage is again read when the specimen reaches the correct temperature. The change in length during heating and cooling should agree within 10 per cent. The actual thermal expansion of a material is measured in thousandths of an inch, and its coefficient is calculated by the following formula:

$$a = \frac{\Delta L}{LT}$$

in which a = coefficient of linear thermal expansion per degree Centigrade;

ΔL = average of changes in length of test specimen due to heating and cooling;

L = length of test specimen at room temperature, ΔL and L being measured in the same units;

T = temperature difference, in degrees Centigrade, over which changes in length of the specimen are measured.

Care should be taken not to disturb the apparatus during the transfer from one bath to the other. The preparation of the sample is also important. If the material is thermosetting, the cure must be complete, as undercured articles have a greater tendency to change dimensions than fully cured parts. The dimensional change

in the case of an undercured article is representative of the coefficient of expansion of the unpolymerized material used to make the article rather than that of the finished article.

Optical Properties

11-50. Index of Refraction.—It is a well-known fact that light travels at different speeds in different mediums. The ratio of the speed of light in air to the speed of light in a material represents the index of refraction of that material. This property naturally applies only to transparent and very translucent materials. There are two methods of finding the index of refraction. The most common method involves the direct measurement of the index of refraction by means of a refractometer. The second method, less widely used but just as accurate as the refractometer method, involves the measurement of the apparent thickness of the test sample by means of light transmission through a microscope.

In the microscopic method the sample is highly polished on one surface and only roughly polished on the opposite parallel surface. The highly polished side is placed face up on the microscope table. The microscope is focused on the rough surface, or bottom side, of the sample, and the longitudinal displacement of the lens tube is recorded. The microscope is next focused on the top, or highly polished side, of the sample, and the displacement of the tube is recorded. The difference between the two readings is the apparent thickness of the sample. The actual thickness of the sample is measured with a micrometer. The index of refraction is calculated by the following formula:

$$\text{Index of refraction} = \frac{\text{actual thickness of sample}}{\text{apparent thickness of sample}}$$

Only those compounds that have some degree of transparency or translucency will have an index of refraction. Opaque compounds such as wood-flour-filled phenolics will not have an index-of-refraction value, but the transparent phenolics will have a value. Table 11-22 lists values for only those plastic materials which have a positive index of refraction.

11-51. Haze.—Probably the most important property of a transparent plastic material is its degree of light transmission. The main function of transparent plastics is to transmit as much

TABLE 11-22

INDEXES OF REFRACTION OF VARIOUS PLASTICS

Material	Index of Refraction
Phenol formaldehyde (molded)	
Transparent	1.5–1.7
Phenol formaldehyde (cast)	
No filler	1.54–1.56
Urea formaldehyde	1.53
Vinyl chloracetate	1.60–1.63
Vinylidene chloride	1.49–1.51
Methyl methacrylate	1.59
Polystyrene	1.47
Ethyl cellulose	1.46–1.5
Cellulose acetate	1.47–1.49
Cellulose acetobutyrate	1.50
Cellulose nitrate	1.47
High acetyl cellulose acetate	

light as possible. In the molding process, certain difficulties which tend to interfere with the transmission properties of the material are sometimes encountered. The plasticizer may sweat, causing fog or haze on the surface of the article, and impurities in the material may cause blind spots in the molded article. To show just how transparent a transparent material actually is, a haze test is employed. Haze is defined as that fraction of the total transmitted light from a beam which is not transmitted in a straight line. It is calculated as per cent by the following formula:

$$\text{Haze per cent} = \frac{T - T'}{T} \times 100$$

in which T = total light transmitted;
T' = amount of light transmitted in a straight line.

The test for haze is run in an enclosed box, as illustrated in Fig. 11-18. The sides, top, and bottom of the box are completely blackened. At one end of the box, a 6-volt automobile-headlight bulb is mounted in front of a silvered reflector. The bulb is enclosed in a cylinder, the inside of which is also blackened. One end of the cylinder is partially closed, having a circular aperture 1 inch in diameter. A simple storage battery supplies the energy to the bulb. Exactly 20 inches away from the aperture is a photo-electric cell.

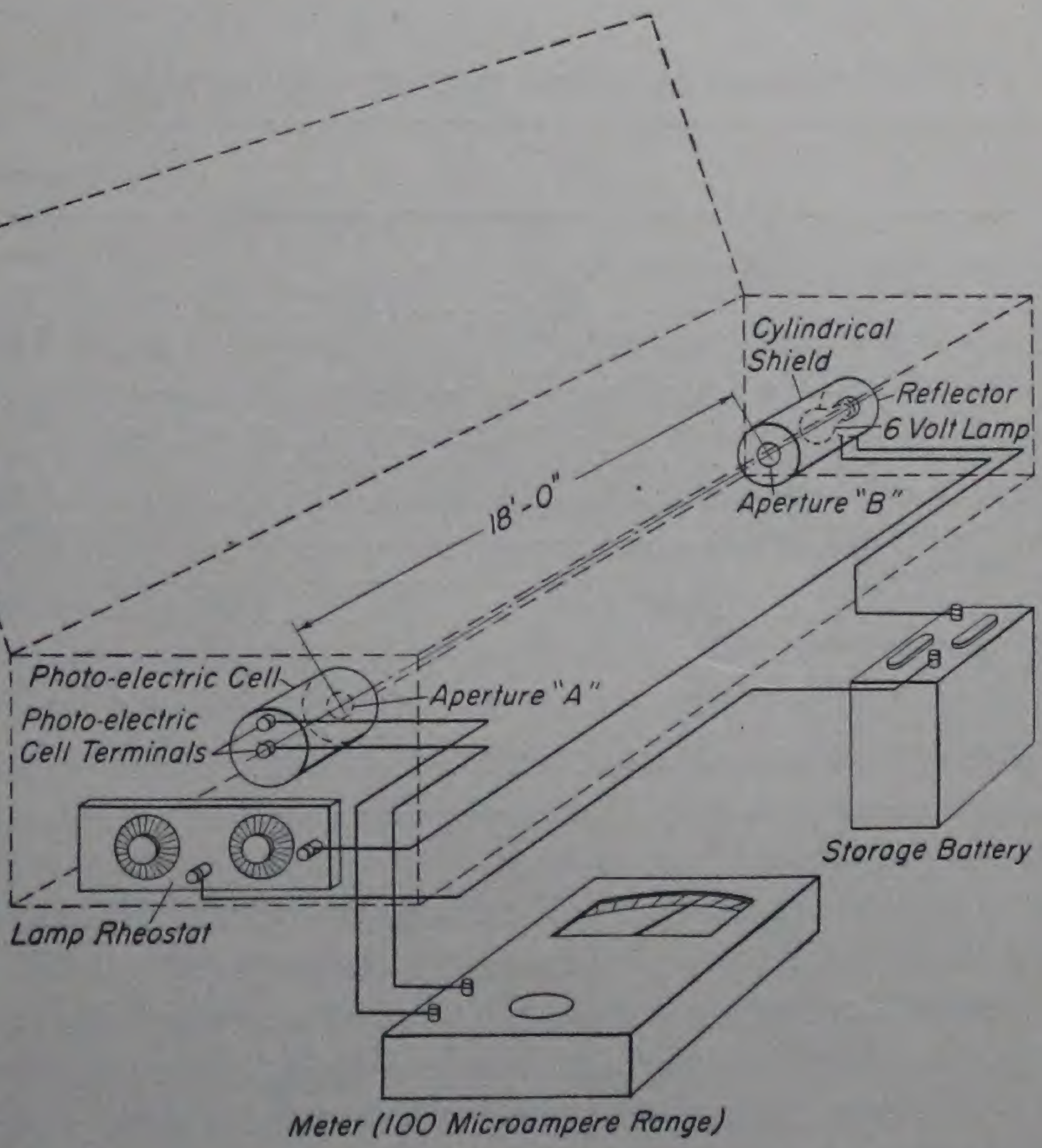


Fig. 11-18. Sectional View of Haze Meter, Showing Apparatus and Connections.

Mounted 2 inches in front of the cell is a blackened disk with an aperture similar to the one in the cylindrical shield at the bulb end of the box. The photo-electric cell is connected to an ammeter of the 100-microampere range, having a 50-ohm internal resistance. The battery is connected to a rheostat so that it is possible to adjust the intensity of the lamp.

The box is closed and the intensity of the light is adjusted by the rheostat so that the ammeter shows a current of 100 micro-amperes. A sample is then placed directly in front of the aperture *A*, which is 2 inches in front of the photo-electric cell, and the ammeter reading is recorded. The photo-electric cell actually records all the light that passes through the test sample and is not deflected at angles greater than 90°. The sample is then placed 18 inches from aperture *A* in front of aperture *B* at the bulb end of the box, and the ammeter reading is again taken. The cell this time

TABLE 11-23

PROPERTIES OF SYNTHETIC RUBBERS

Material	Specific Gravity	Tensile Strength Pounds per Square Inch	Elongation Per Cent
Neoprene	1.24	1,600–1,750	400–435
Vistanex	.91	3,000–3,400	780–820
Polythene	.92	1,900	600
Buna S	.94	3,000–3,400	640–660
Perbunan	.96	3,500–3,800	600–640
Thiokol A	1.60	780–800	360–380
Thiokol B	1.34	1,100–1,500	470–530
Buna 85	1.03	3,600–3,800	640–660
Vinyl chloride	1.4	1,200–1,500	400–500

records all the light subtended by the aperture but does not record the scattered light. The thickness of a sample of the test specimen shall be as received or, for comparative purposes, shall be .125 ± .005 inch. Care must be taken to remove dust and grease from the test specimens before testing.

Properties of Synthetic Rubbers

11-52. All the synthetic rubber materials may be classed chemically as plastics. However, the synthetic rubber materials are very seldom found in a plastics molding plant. Rubber working is an industry in itself, but no book on plastics is really complete unless it contains information on the chemistry and properties of synthetic rubber materials. The physical properties discussed under synthetic rubbers are, in general, the same as those for the common plastic molding materials; therefore, it is not necessary to define the various properties.

No details of the test methods for rubber compounds will be given here. Because of the extensibility and flexibility of such compounds, it was found that the standard testing methods and machines for common plastic materials did not give satisfactory results. For that reason, many special testing machines have been devised and are in daily use in testing rubber products. Results that were obtained by the use of such special machines are shown in Tables 11-23 and 11-24. Table 11-23 gives the specific gravity, tensile strength, and elongation values for the various types of

TABLE 11-24

PROPERTIES OF SYNTHETIC RUBBERS

Material	Abrasion Resistance	Safe Application Temperature Degrees F	Dielectric Constant
Neoprene	Excellent	300	7.5 at 1,000 cycles
Vistanex	Good	270	2.29 at 1,000 cycles
Polythene	Excellent	200	2.3 at 1,000 cycles
Buna S	Excellent	300	4.4 at 60 cycles
Perbunan	Excellent	300	15.0 at 60 cycles
Thiokol A	Fair	200	
Thiokol B	Fair	200	
Buna 85	Excellent	300	14.0 at 1,000 cycles
Vinyl Chloride	Excellent	200	5.5 at 1,000 cycles

synthetic rubbers. Table 11-24 gives their abrasion resistance, safe application temperature, and dielectric-constant values.

Chapter Twelve

Molds for Plastic Products

12-1. Introduction.—Plastic materials and molds are partners in the business of producing plastic articles. The material in the molding-powder state is shapeless, and it remains for the mold to convert it into a recognizable article. In a broad sense, a mold may be defined as a matrix in which the plastic material is formed. When a plastics molder uses the term *mold*, he does not refer only to the cavity, or form, that shapes the article, but rather he means all the individual parts that go along with the cavity.

12-2. Functions of Molds.—The primary function of a mold is to form the plastic article. In the actual shaping of the article, however, the mold performs several functions. It acts as a container, or holder, for the plastic material. To form a plastic article, both heat and pressure are required. When the pressure is applied to the mold full of material, the material tends to flow and escape from the mold. If too much of the material escapes, the article cannot be formed completely. Molds are constructed so as to confine, or restrict, the actual loss of material. The mold is indirectly the source of pressure. Although it is true that the pressure applied to the plastic material in a mold comes from a motor or an accumulator, the actual pressure is nevertheless applied by the walls of the mold. The material is sandwiched between the walls of the mold, and is so compressed. Provision must be made in the mold itself for the source of heat, which may be steam, electricity, or oil. Some molds are heated indirectly by conduction, but this method is definitely inefficient.

12-3. Requirements of Molds.—A fundamental property of all plastic materials is that they faithfully copy and reproduce the mold, even to its polish. To produce bright shiny plastic parts, the mold must have a high polish, which it must retain. One of the accomplishments of the plastics industry is accurate mass production. If finished articles are expected to gage to within a few thousandths of an inch, the mold itself must be absolutely accurate.

The mold must also be strong enough to withstand the pressures used in the various methods of molding. Since the mold is the prime tool of the custom molder, it must be mechanically perfect in order to insure good quality and efficient production.

The essential consideration in designing a mold is that the mold be adequate for the material to be used in the molding of parts. Because of wide variations in the properties of materials, the designer must investigate and determine the type of material to be used. For example, the bulk factors of plastic materials vary a great deal, the minimum being about 1.5 to 1 and the usual maximum about 12 to 1. Bulk factor is the ratio of the volume of the loose molding powder to the volume of the finished molded article. As a result, a mold designed for the use of material with a bulk factor of 1.5 to 1 could never be used to mold material with a bulk factor of 12 to 1. Simplicity of mold and simplicity of operation are also essential points of mold designing. Unnecessary side cores and excessive handling of loose pieces retard production and, as a result, increase the cost of the finished product.

12-4. Importance of Molds.—The mold designing and building stage can make or break the molder. Molds are expensive, some of them costing as much as $15,000. If the dimensions are incorrect or if some feature of construction is impractical, it is possible that the articles produced from that mold will be useless. The building of the mold is a skilled craft. One false cut in the steel may well mean starting all over again. The dimensions of a machined mold might be perfect, but the heat treatment to harden the mold might cause distortion.

Of the many steps necessary to produce a plastic article, the manufacture of the mold is by far the most significant. The exact duplication of a metal item in plastics is often impossible, and in most cases is impractical. Articles to be made from plastics must be designed for plastics. It is, therefore, necessary to consider not only the properties of the plastic material but also the ability to mold. The combination of metal and plastics is today a common occurrence. Ordinary plastic drawer pulls have metal inserts, and automobile steering wheels are molded in plastic over a metal core. In metal and plastic combinations, ways and means of anchoring the metal parts during the molding process present problems in mold

design. Materials and molds with regard to design of the article will be discussed fully in Chapter 13.

12-5. Mold Types.—Molds may be classified in several ways. According to the easiest and most general method of grouping, molds are of hand, semi-automatic, and fully automatic types. This particular grouping is based on the action of the mold rather than on the detail of the mold. For example, a hand mold is one that is removed from the molding press after the completion of each molding cycle. The mold is taken apart, the piece is ejected, and then the mold is put together again and replaced in the press. The term *fully automatic* means that the mold is stationary in the press while the molded article is ejected by any automatic means. Hand molds are the least efficient, since taking them out of the press and putting them back causes a loss of heat that must be replaced before additional molding is performed. The hand-type mold finds its greatest use in the single-cavity die for sample purposes. In certain cases where the volume of business is too small to warrant the building of a multiple-cavity die, the hand mold is employed. Weight is a factor in any mold. For example, since a radio-cabinet mold weighs several hundred pounds, it would be impractical to use the hand-type mold, as an overhead crane would be needed to remove the mold. In general, most plastic molds are of the semi-automatic or fully automatic type.

Another method of classifying molds is by the type of material used in conjunction with them. For example, thermosetting materials are usually molded by compression molding, whereas thermoplastics are molded by injection molding. Thermoplastics may be compression molded, but this process is slower and therefore more costly than injection molding. Compression molds are, in turn, divided into three different types: the flash mold, the semi-positive mold, and the positive mold. Each type has definite reasons for existence. There are many variations of semi-positive molds, the two most important of which are the transfer mold and the split-cavity mold. Injection molds are all more or less flash molds; however, the inherent construction is different from that of the compression flash mold.

12-6. Steel Molds.—The materials used to construct molds must be selected very carefully. Because a high pressure is exerted on the walls of the molds during the molding cycle, the material

almost universally used for the construction of plastic molds is some variety of steel. For a number of years, however, there has been a difference of opinion as to the best kind of steel to use. Tool steel, such as the oil-hardened type, is used to good advantage in many cases. In other cases, mild machine steel that is properly heat-treated renders excellent service. Although tool steel undergoes minimum distortion during heat treatment and under molding pressures, it has the disadvantages of being difficult to machine and costing more per pound. Machine steel is much easier to machine and costs less per pound, but it has the disadvantages of distorting under heat treatment and of cracking under molding pressures, because of its hard surface and comparatively much softer core.

The chemical compositions and quality requirements specified for steel for molds continued to increase until there were many thousands of types of steel for various applications. This condition, being a matter of concern in the steel industry for years, prompted the General Technical Committee of the American Iron and Steel Institute (A.I.S.I.) to make a study of the various types of steel with a view to simplifying the problems of both consumer and producer. Realizing the benefits of standardization and simplification, their first objective was to determine which grades of steel were the ones in most common demand and the practicability of combining specifications having like requirements. The survey convinced steel producers that, if they produced a limited number of specifications, deliveries could be expedited and service improved. As a result, the General Technical Committee published a list of selected grades of steel, representing compositions of proved merit and extensive use for a wide variety of purposes. The Society of Automotive Engineers (S.A.E.) has also published a set of specifications for the same purpose.

Since there are many thousands of different plastic applications, it is almost impossible to classify mold steels for each type of application. Each application must be studied separately, and the particular type of steel that best suits its qualifications should be chosen. The method of molding is also an important consideration in selecting the type of steel to be used in mold construction. To a lesser degree the size of the mold can influence the choice of steel. Three typical steel formulas for various uses are as follows:

Type 1.—General-Purpose Steel:

Element	*Per Cent*
Carbon	.10
Manganese	.50
Phosphorus	.03
Sulfur	.03

Type 2.—Strain-and-Service Steel:

Element	*Per Cent*
Carbon	.10
Manganese	.40
Chromium	1.50
Nickel	3.50

Type 3.—Dimensional-Accuracy Steel:

Element	*Per Cent*
Carbon	.90
Manganese	1.60
Silicon	.25

Steel molds are expensive to make and, in many instances, the mold cost has discouraged the manufacture of an article from a plastic material. It is true that steel molds are durable, but in most cases they outlast the production of the article they manufacture. This actually means that the manufacturer is paying for a mold, the full value of which is never realized. There is no set rule as to the number of molded parts that may be made from a single mold, since many variable factors are involved. The type of material that is used, the temperature and pressure used in molding, and the number of articles produced are all factors that affect the life of the mold and the cost of the finished article. For example, a manufacturer may require 250 balance pans, which are resistant to hydrofluoric acid, for a special type of weighing scale. A steel mold is built at quite an expense to the manufacturer, and the 250 balance pans are produced; but the cost of the individual pans is high because of the small volume produced from the mold.

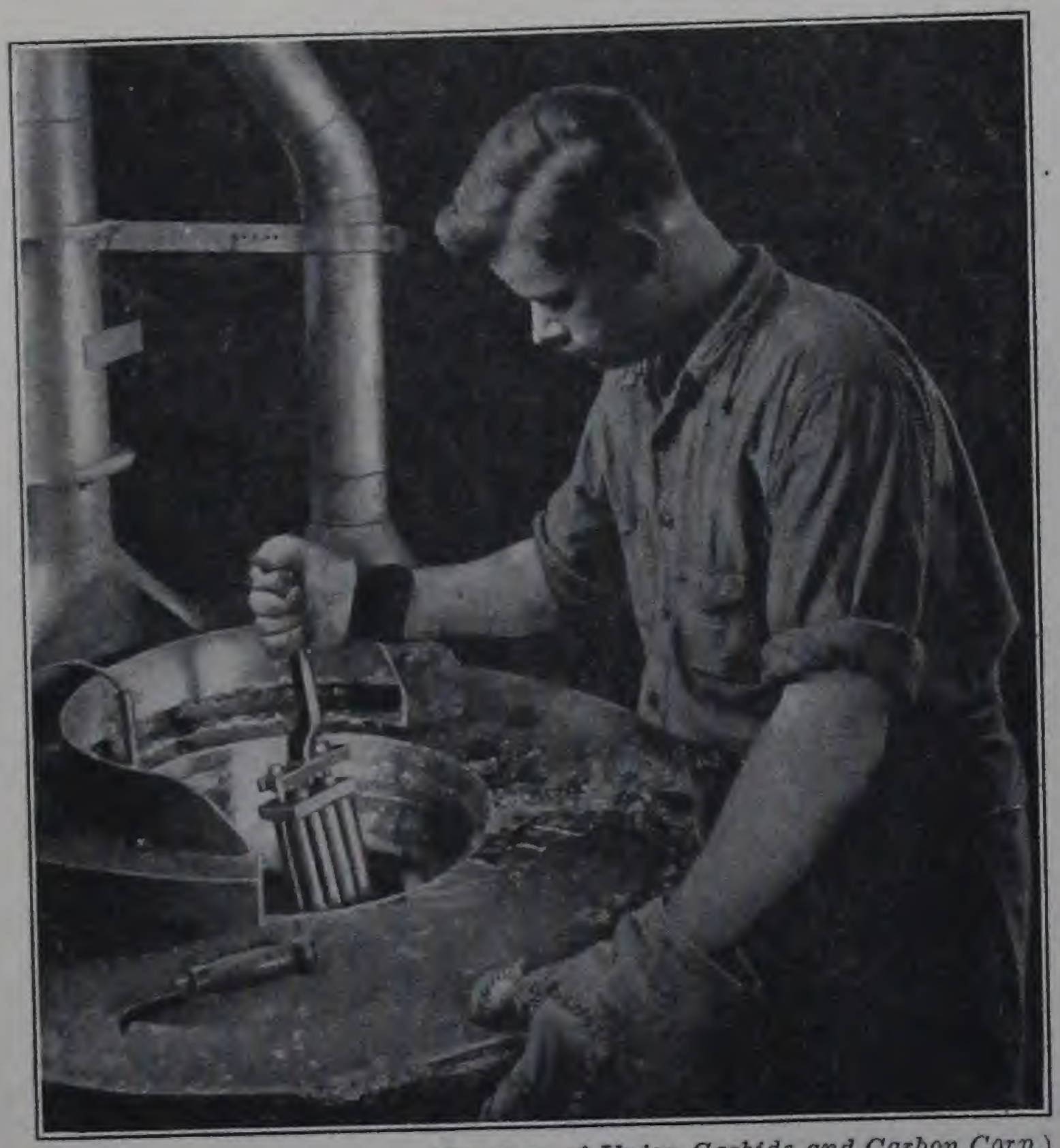
12-7. Short-Time Molds.—A short-time mold is one that produces relatively few pieces and then becomes obsolete. It is no

secret that mold costs are a distinct disadvantage to the molding industry. Tool and die makers have been constantly searching for a material other than steel to make what the industry calls short-time molds. The button industry is an excellent example of where short-time molds would find good use. Since styles change rapidly, each successive season requires new molds for new styles of buttons. As a general rule, the steel molds built for buttons for the preceding season are in excellent condition, but they must be discarded because they are outmoded.

New materials have been produced for short-time molds, but up to date none has been a complete success. Beryllium-copper alloys have unusual strength and may be cast, but certain disadvantages have prevented their use for even medium-sized molds. Attempts have been made to cast steel into a mold rather than to machine the steel into a mold with little success. Another method of mold making, still in the experimental stage, is the metal-spraying process. This method constructs the cavity part of the mold by successive sprayings of metal over a master model. The sprayed blank is then reinforced by cast steel. Research is continuing in an attempt to find a cheaper and quicker method of making molds.

12-8. Lead Molds.—In contrast to molded products, cast products are formed in lead molds, which are inexpensive to make and are ideal in that, when the casting is removed, the lead is remelted and made into another mold. The initial step in preparing a lead mold for casting is the shaping of a suitable die. The die, which is made from a piece of steel, has the same shape as the plastic part to be manufactured. Every die must have a slight taper from one end to the other, in order to permit the removal of the die from the mold and the withdrawal of the casting from the mold. The dies should be hardened because they are used many times, and they should have polished surfaces because the surfaces determine the finish of the casting.

The lead molds are made by dipping arbors or single dies into molten lead, as shown in Fig. 12-1. In the case of simple shapes, several dies are mounted together on a single arbor plate so that the molds may be made more quickly. The cold arbor chills the portion of lead which comes in contact with it and, when it is removed, a lead shell clings to it. Because of the tapered dies, the



(Courtesy of Union Carbide and Carbon Corp.)

Fig. 12-1. Dipping Steel Arbor Into Molten Lead to Form Lead Mold.

molds may be removed from the arbor very easily. When cool, the newly formed lead molds are ready to receive the cast resin.

12-9. Mold Making.—The metal used in mold construction must have the following properties:

1. It must take a hard surface in order to withstand high pressures and continued operation.
2. It must remain resilient below the hardened surface.
3. It must be unaffected by temperatures as high as 350° to 400° F.

In general, the two most common methods of mold making are machining and hobbing. In machining, the mold is simply carved from a block of steel. The carved mold is then case-hardened and polished. In addition, the majority of molders chromium-plate the mold to protect it from wear and corrosion. The process is long and tedious and, as a general rule, is used only when the total number of cavities and force plugs to be machined is small. The hobbing process is used mainly when there are many cavities to be made. The hobbing process, as compared to machin-

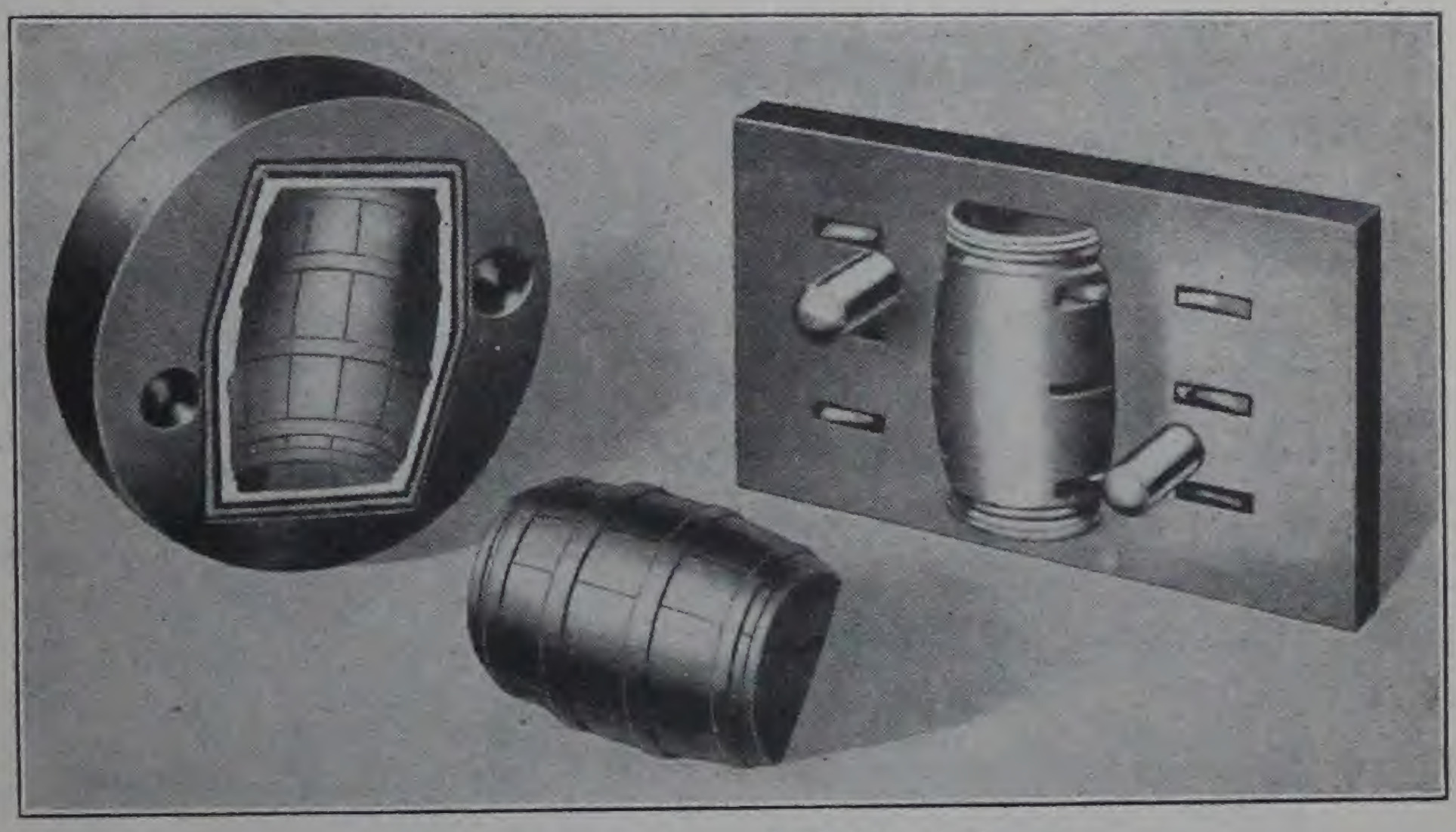


Fig. 12-2. Hob and Hobbed Cavity.

ing, is relatively inexpensive and should be used whenever possible.

12-10. Hobbing Process.—The hobbing process requires a master sample, which is always machined from steel. The hob, which is an exact replica of the article, is usually made from tool steel, chrome-vanadium steel, or other special alloy steel that, after heat treating, is extremely hard and tough. An illustration of a hob and a hobbed cavity is shown in Fig. 12-2.

The principle of hobbing is to force a hardened-steel master into a blank of very soft steel. The hob, as well as imparting shape to the blank, also imparts polish; therefore, the hob itself should be highly polished. In some cases, the hob is even chromium-plated. The size and shape of the steel blank depend on the size of the cavity to be made, the size of the hob, and the amount of metal to be displaced. The regular laws of compression apply to metals in the hobbing process; therefore, the blanks for hobbing usually receive special treatment and certain preliminary machining. In order to reduce the amount of metal flow, most of the metal is removed from the back of the blank by drilling or milling. This makes room for the actual metal displaced during the hobbing operation. In order to eliminate flow lines and secondary polishing operations, it is desirable to sink the hob with a single continuous stroke.

The hobbing process differs from forging in that the work is done at ordinary temperatures, and the hob is sunk slowly under continuous, heavy pressure, with complete absence of impact.

Shallow dies may be satisfactorily produced in such a way but, since the flow of metal in the blank is accompanied by a certain amount of lateral displacement, the use of such dies is limited to the production of articles where close tolerances are not essential. The demand for deeper dies and close tolerances usually required by plastic molding forced an improvement on the original hobbing process.

In order to produce accurate and deeper dies, a heavy chase ring is used to confine the blank laterally. The chase, or retainer, ring consists of a steel forging having a cylindrical hole and fitted with a hardened-steel bushing. When using the chase, the blank, in the form of a disk that has a sliding fit in the chase, is placed in the cylindrical hole so as to rest on the bottom platen of the press. The hob, which also has a sliding fit in the chase, is placed in the cylindrical hole so that its face is in contact with the blank to be hobbed and so that its base bears against the upper platen of the press. In this way, the metal displaced in the blank, which is constrained against lateral flow by the chase, flows up the side of the hob. Dies produced by this method are exact duplications of the hob. This improvement in hobbing accounts for the fact that die hobbing now holds an indispensable position in mold building.

12-11. Size and Shape of Hobs.—The die blanks are usually circular. This shape allows the greatest economy in material, offers the best machining preparation, and, in most multiple-cavity molds, is the easiest shape of die to hold in place. In addition to these advantages, if the hobbing is to be done in a chase, the circular shape is most easily prepared to fit the cylindrical hole of the chase. Since the disk is confined in the chase, its diameter need only be large enough to give the required wall thickness plus whatever excess may be needed to allow for any subsequent machining.

Occasionally, relatively long and narrow dies, which for reasons of precision require the use of a chase, are to be hobbed. In order to avoid the excess of material inherent in a disk of sufficient diameter for such a die, the blank may be of the same general appearance as the die cavity. It is only necessary that the ends of the blank be circular in order to fit the chase. The spaces between the sides of the blank and the chase are filled with two hardened-steel blocks, as shown in Fig. 12-3. These blocks, which

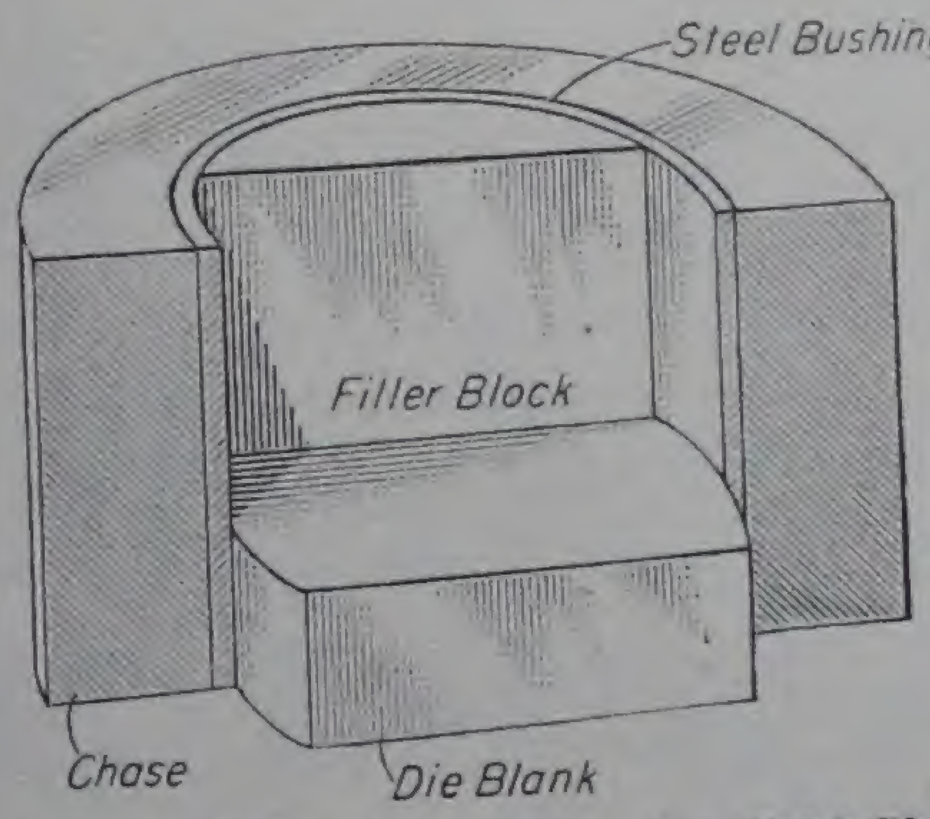


Fig. 12-3. Hobbing Apparatus for Odd-Shaped Dies.

extend to the top of the chase, prevent spread of the die blank and serve as guides for the butt of the descending hob.

12-12. Heat Treating of Steel.—The hardening of the hob is essential in order to prevent its deformation under pressure. Although the particular operation depends on the kind of steel used, it is more exacting than most hardening operations and requires greater care. Tool steel is primarily soft, in which condition it is not satisfactory to use in the molding operation, because high pressures and high temperatures would soon distort and deform the mold. The steel must be hardened. Heat treating of steel controls the carbon structure of the steel and, hence, the physical properties. The structure of ordinary high-carbon tool steel is different at high and low temperatures. The change of structure takes place very gradually at ordinary temperatures, but rapidly at high temperatures. The crystalline change requires about 20 seconds at red heat. If high-carbon steel is heated to red heat and then is allowed to cool very slowly, the internal-structure change takes place while the steel is still very hot. When the steel has finally cooled, it will be soft. This general process is known as annealing. In order to harden steel, it is necessary to chill the steel very quickly after the heating. This is usually done by plunging the steel into cold water, this operation being known as quenching.

The actual amount of hardening of a steel by heat treatment depends on its carbon content. The greater the amount of carbon, the greater the hardening effect by heat treatment. A low-carbon machine steel must have the carbon content increased before it is possible to effect any appreciable hardening. Low-carbon machine steel at high temperatures is permeable to carbon gases. The

method of gassing metal is known as pack-hardening, or case-hardening. Bone dust or charcoal is placed in an iron box with the sample of steel to be hardened. At high temperatures, these materials give off carbon monoxide, which penetrates the steel to a depth of approximately $\frac{1}{32}$ inch. This process, known as carburization, continues until the carbon content of the outer layer of the sample to be hardened approaches saturation. After carburizing, the sample is allowed to cool in air. It is then reheated to approximately 100 degrees above red heat and again is allowed to air-cool. The steel is again heated to red heat and finally is quenched.

There are many different methods of hardening steel. In some cases oil is used as the quenching medium, and in other cases brine is used. Cyanide is also used as a hardening material. Different steels require different lengths of time to reach red heat, some requiring greater heat than others. Where steel is to be hardened, it is always best to get the complete details of heat treatment from the manufacturer of the particular grade of steel being used.

12-13. **Mold Polish.**—Most of the plastic parts being manufactured at the present time have a high surface polish. Since plastic materials faithfully copy even the polish of the mold, it can be assumed that the molds making these various plastic items are highly polished. A steel surface may be made mirror-bright by simply buffing and polishing it with various wheels and compounds. This type of polish, however, does not last long when placed in contact with various plastic powders. Although it is true that most of the modern plastic materials are free from ingredients that are injurious to steel, it has been found that, when different types of materials are molded alternately, there is evidence of pitting and loss of luster. Very frequently, troublesome sticking results. These conditions may be eliminated by plating the mold surface with chromium.

12-14. **Mold Plating.**—Chromium-plating of a mold, while it does not guarantee the elimination of sticking of material, reduces the difficulty a great deal. Molds are plated to reduce surface wear, reduce sticking and surface poisoning tendencies, reduce surface friction, and increase the surface brightness of the molded piece. A thin film of chromium applied to a solid steel mold presents a very hard surface. The wear produced by abrasive

particles in the plastic material is less pronounced on a chromium-plated mold than on an unplated one. Chromium is a slippery metal, and plastic materials meet less resistance in flowing over a chromium surface than over an ordinary steel surface.

Chromium-plating is a study in itself, but in general two types of chroming are used in conjunction with plastic molds, namely, flash plating and hard plating. Flash plating results in a chromium thickness that never exceeds .0005 inch. This type of plating is used where only a small volume of plastic articles is expected from the mold. In hard plating, the thickness of the film of chromium varies from .005 to .030 inch. This type of plating is used for large volume production where the wear and tear on the mold is likely to be serious.

In any type of chromium-plating, the steel surface must be free from foreign matter, particularly grease. Chromium-plating is accomplished by electro-deposition. In order to insure a uniform chromium surface on the mold, the electrode must be so placed that the distance from it to every part of the mold is uniform. When the mold to be plated is complicated in shape, a series of wire electrodes is used. The series consists of one main lead-in wire to which are attached many other sprawling wires that are bent to take care of the shape of the mold. The trick in chromium-plating is to plate slowly, so that a firm bond is obtained between the chromium and the mold.

If the strength or the temperature of the chromic-acid solution is too high, or if the current density is too great, a spongy chromium-plate results. This spongy plating peels away from the mold, with the net result that the mold has no film of chromium. If chromium-plating is done properly, the mold, when removed from the plating bath, will be bright in appearance. If the surface appears cloudy or milky, the mold should be dechromed by a hydrochloric-acid bath, and the operation should be repeated. The usual temperature for chromium plating is approximately 100° F. The current density should be controlled throughout the plating operation. Table 12-1 indicates the time in hours and the amperes per square inch required to produce a film of chromium .001 inch thick.

12-15. Engineering of Mold Making.—The importance of the mold cannot be stressed too much. The technique of molding may

TABLE 12-1

CHROMIUM-PLATING REQUIREMENTS

Time Hours	Amperes Per Square Inch
.5	3.25
1	2.25
2	1.3
4	.90

be perfect and the plastic material may be as nearly perfect as possible; but, if the mold is impractical or dimensionally incorrect, the molder is in for a bad time. Every mold is made from a blueprint, which is the result of careful consideration of the design of the article and the characteristics of the plastic material. The shrinkage factor of the material must be known before the blueprint can be made, as shrinkage of a material is very important in the dimensional consideration of the mold. The bulk factor of the material must also be ascertained to insure enough loading space in the mold. If inserts are to be used in conjunction with plastics, consideration must be given to the anchoring of the insert in the mold while the pressing operation is going on. The expansion and contraction of the insert must be correlated to the wall thickness of the plastic article so as to guard against cracking of the plastic. These and many other problems are discussed in greater detail in Chapter 13.

12-16. Compression Molds.—Before going into the details of construction of the various types of compression molds, it is well to outline in general the make-up of a mold. Molds are always divided into two parts. One part has the outside shape of the article to be made; the other part has the inside shape of the article. For example, if a water tumbler is to be made from a plastic material, the bottom part of the mold is shaped exactly like the tumbler, and the top part of the mold is also shaped like the tumbler, but the dimensions of the top part are smaller than those of the bottom part. The difference between the dimensions of the top and the bottom parts of the mold represents the wall thickness of the tumbler. The top part of any mold is known as the top force or the plunger, and the bottom part of the mold is known as

the bottom force or the cavity. A mold may contain any number of cavities, but every cavity must have a corresponding top force.

The number of cavities in a mold is determined by the requirements of the customer and the economics of mold construction. The top force is always mounted on a steel block that is cored for the heating medium. In some cases where the force is large, it is cored for the heating medium. The individual cavities that go to make up the bottom part of the mold are mounted in a chase, or cavity block, which is cored for the heating medium. The bottom half of the mold has dowel, or guide, pins mounted in the cavity block. Holes in the top-force block correspond to the dowel pins in the lower half of the mold. The dowel pins and the holes are for the express purpose of alining the die.

The ejector, or knockout, mechanism is mounted directly below the lower half of the mold or directly above the top half of the mold, its position depending on the circumstances. If a molded article has no undercuts or anchoring inserts, it can be made to stay in either half of the die. For example, consider a dashboard panel for an automobile that is made from a plastic. Since the top force actually represents the back of the panel, the ejector-pin, or knockout, marks should be where they cannot be seen, or on the back. In this example, the panel is made to adhere to the top force, above which is mounted the knockout mechanism.

12-17. Knockout Mechanism.—There are many types of knockout mechanisms, and it is safe to say that each mold requires some type. A typical example of a simple knockout mechanism is the pin-bar knockout. Examination of any two-hole or four-hole plastic button will usually reveal a small round imprint between the holes on the back of the button. This imprint is made by the knockout pin. The ordinary compression-mold button cavity has a hole in the center. When the mold is installed in the press, a pin bar is fitted below the mold so that the pins mounted on the bar come up through the holes and are flush with the bottom surface of the cavity. After the button has been molded, the bar is lifted by mechanical means on the sides of the press. This has the effect of pushing the pin against the button and pushing the button out of the cavity. The size of the knockout pins is determined by the size of the object to be ejected. In many cases, more than one knockout pin is used for each cavity.

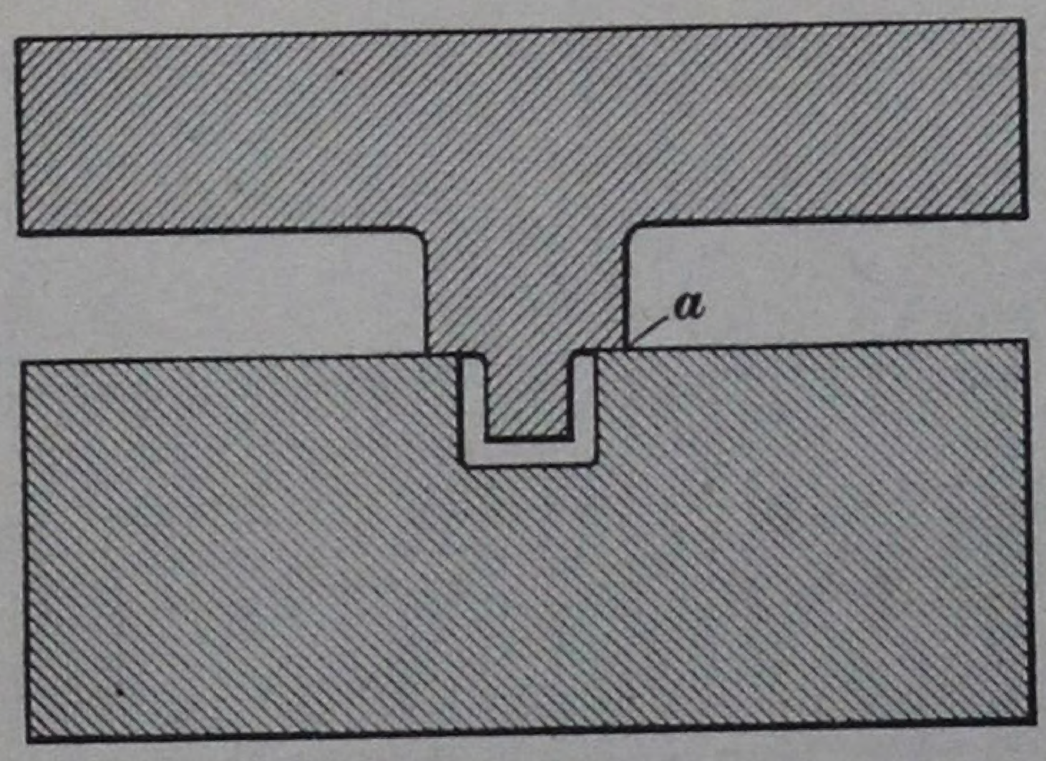


Fig. 12-4. Flash Mold.

12-18. Flash Molds.—The flash type of mold, Fig. 12-4, which is usually the least expensive type, is used in producing thin pieces and where preforms are used as the charge. This type of mold must have relief around the cavity on either the lower or the upper part of the mold, so that there is only a comparatively small area in contact when the mold is completely closed. The land, or cut-off, area *a* should not be reduced too greatly, because the high pressure used during the molding cycle will upset or ruin the mold. On the other hand, the cut-off area should not be too great, as there will then be heavy flashing, which increases the cost of the finished part. Any material that escapes from the die during the pressing operation is called flash, or waste.

By examining the flash mold, it will be noted that there is no apparent means of confining the material. The plastic material is loaded into the bottom cavity. When pressure is applied to the top force and the mold starts to close, the top force comes in contact with the plastic material. The material seeks to escape and flows upward in the space between the top force and the bottom cavity. As the pressure increases and as the mold comes nearer and nearer to closing, the material comes nearer and nearer the top of the mold. Before the mold can actually close, some of the material escapes. The material that escapes is pressed between the mounting block of the top force and the chase of the bottom half of the mold. When the molded part is removed from the mold, it carries with it a ring of flash around the top rim.

It is always necessary to use more material in a flash mold than the net weight of the article to be made, because it is this excess material that insures sufficient back pressure during the

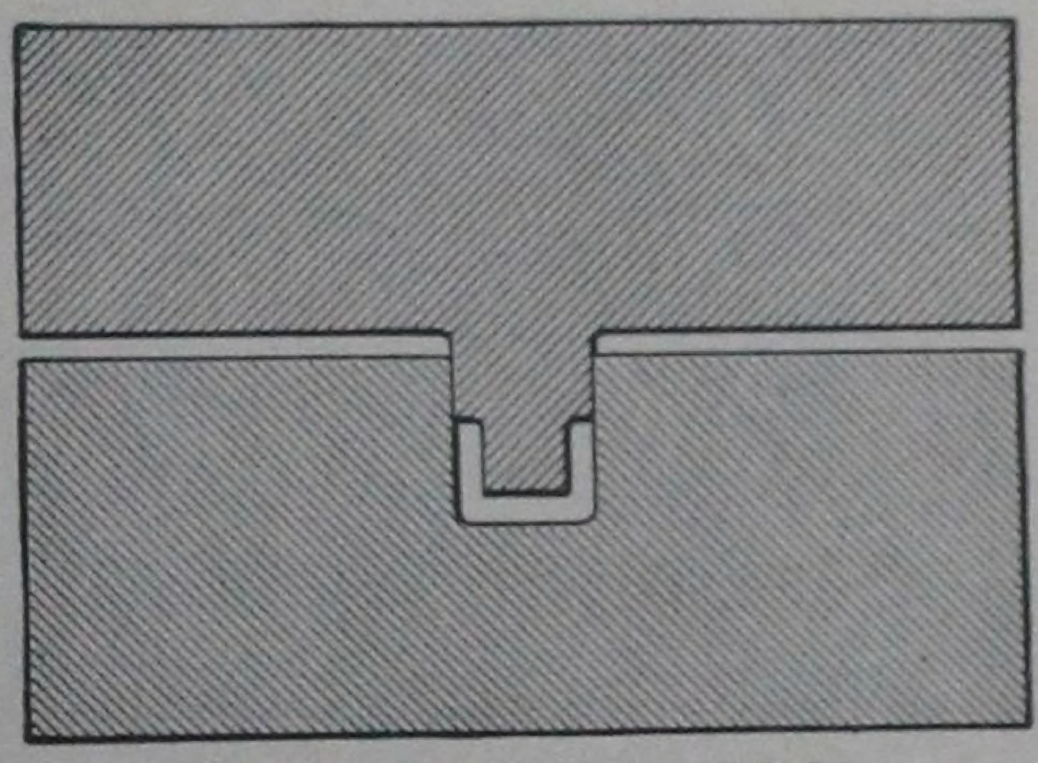


Fig. 12-5. Positive Mold.

molding operation to guarantee a fully molded article. The name *flash mold* is derived from the fact that the objects molded from this type of mold always have a flash rim around the parting edge of the die.

A flash mold cannot be used for every type of application. For example, it is impracticable to use a flash mold for making a water tumbler from a plastic material having a bulk factor of 12:1. Not enough material could be placed in the cavity to press out the tumbler, since there is not enough space in the mold to accommodate the required amount of powder. Articles of deep draw are, as a rule, not made by using a flash mold, because too much of the powder escapes before the mold is closed.

Intricately shaped articles and applications that require good density cannot be made in flash molds, owing to loss of pressure. The loss of pressure is very important; as a matter of fact, a flash mold may be defined in terms of pressure. A flash mold is one in which the material is under a gradually increasing pressure, the climax being reached when the mold is fully closed. The material is never under full pressure, since it is flowing and moving in an unconfined space. Even when the mold is fully closed, the full pressure is not exerted upon the material that is forming the article, because some of the pressure is dissipated on the flash ring. This definition should be studied thoroughly and compared with the definition of semi-positive and positive molds in the succeeding paragraphs.

Flash molds have advantages over molds of other types in that they are cheap and offer little difficulty in production. Molding cycles for flash molds are likely to be faster than those for other types of molds. Probably the greatest disadvantage of the flash